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# AN IMPROVED RESPIRATION CALORIMETER FOR USE IN EXPERIMENTS WITH MAN

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## INTRODUCTION

The nutrition of the human body consists mainly in the transformation of food into body material and the ultimate transformation of the energy potential in both food and body material into such forms of energy as heat and muscular work. The transformations of both food and body material occur largely in accordance with the needs of the body for energy. To understand the laws governing the nutrition of the body, knowledge regarding these transformations of matter and energy is essential.

To obtain such knowledge it is necessary to have some means of determining the intake and output of both matter and energy by the body. This involves the use of some form of apparatus that will give an accurate measurement of the gaseous exchange and the energy production of the body. Such an apparatus is the so-called respiration calorimeter employed in connection with the nutrition investigations of the Department of Agriculture.

The first apparatus of this kind constructed in this country was developed in connection with these investigations. Work on this device was begun in 1892 by Prof. W. O. Atwater at Wesleyan University, Middletown, Conn. When the Department of Agriculture undertook an inquiry into the food and nutrition of man in 1894 as a logical outgrowth of the earlier work of Prof. Atwater for the Smithsonian Institution and the United States Department of Labor, the need of some means of determining the income and outgo of matter and energy in the body was recognized, and the general plan of work to be undertaken as part of the inquiry was made to include experiments with the respiration calorimeter which had been devised for measuring factors of outgo.

For use in the study of the output of matter by the body, the device was similar in principle to the respiration apparatus of Pettenkofer(16),[1]

[1] Reference is made by number to "Literature cited," p. 346-347.

with alteration in detail in accordance with modification in methods of investigation, but in its equipment for the measurement of the output of heat it was quite original. Prof. E. B. Rosa, then of Wesleyan University and associated with Prof. Atwater in the investigations, devised a method of preventing the passage of heat through the walls of the respiration chamber, and provided for carrying out and measuring the heat generated within it. The term "respiration calorimeter" was applied to the Atwater-Rosa device to indicate that it performed simultaneously the functions of both a respiration apparatus and a calorimeter.

Experiments with the respiration calorimeter have been continued as part of the nutrition investigations of the Department of Agriculture during the 20 years or more since they were begun. With the progress of the work many modifications have been introduced for the purpose of making the apparatus simpler, easier, and more economical to operate than the original, while yielding more complete and more accurate data. Descriptions of the apparatus in its original form and its later modifications, and the results of a large number of experiments with it, have appeared in former publications of the Department (1, 2, 3, 4, 6, 9) and have become a part of the data commonly included in textbooks and works of reference.

As a result of the work of Atwater and his associates, the investigator has been provided with an apparatus of precision and a method of investigation which, with adaptation in different laboratories to meet varied experimental conditions, have proved valuable for a range of work even wider than was originally anticipated. In the nutrition laboratories of the Department of Agriculture it has been employed in the form described in the present publication in studies of the utilization of food and the performance of muscular work, and a recent development, to be described in detail in a later publication, has been adapted to studies of problems in plant physiology. At the Institute of Animal Nutrition, State College, Pa., Dr. H. P. Armsby employs a respiration calorimeter, which he has adapted from the original Atwater-Rosa type of apparatus, in investigations of the nutrition of farm animals conducted in cooperation with the Department of Agriculture. In other inquiries besides those of the Department respiration calorimeters have proved of great value in investigations of different but related character. Investigators have modified and improved the original form to suit their special needs, though this method of research has long passed the experimental initial stage and has become recognized as possessing great possibilities where accurate measurements of energy values and gaseous exchange are needed to supplement the data which the investigator secures by other methods.

The respiration calorimeter employed at the present time in the nutrition investigations of the Department of Agriculture is a development of

the one used for over 12 years in the laboratory of Prof. Atwater. In 1907, when because of illness he discontinued his connection with the research, the respiration calorimeter was transferred to Washington. To move the apparatus it was necessary to dismantle it completely, so that to set it up again in the laboratory provided for it in the new building of the Department involved its practical reconstruction. Advantage was taken of the opportunity thus afforded to modify it in many important details, with special consideration for simplicity of structure and convenience of operation. The reconstructed apparatus has been briefly described in a former publication of the Department (15) and elsewhere (14). The experience with this apparatus has suggested further improvements that have been incorporated from time to time, with the result that the work of conducting an experiment with the respiration calorimeter is much less than formerly, and a degree of accuracy of measurement is obtained that was not possible with the apparatus in its earlier state. The present publication describes this greatly improved respiration calorimeter in detail. A general view of the apparatus is shown in Plate XXX.

## PRINCIPLE OF THE RESPIRATION CALORIMETER

The principle of the respiration calorimeter now in use in the nutrition investigations is the same as that of the later form of the apparatus employed in the investigations formerly conducted at Wesleyan University. For the determination of gaseous exchange the device is similar to the respiration apparatus of Regnault and Reiset (17), having a respiration chamber and a system of air-purifying devices connected in series in a closed circuit. The air confined in the circuit is kept in circulation, the respiratory products imparted to it by the subject in the chamber being constantly removed and oxygen constantly supplied to replace that used by the subject. For the determination of heat produced in the chamber the device is a constant-temperature, continuous-flow, water calorimeter, in which the calorimetric features of the original Atwater-Rosa apparatus are retained. These provide for preventing the passage of heat through the walls of the chamber and for taking up the heat by a current of cold water as fast as it is generated in the chamber. The determination of respiratory exchange and energy transformation, to be of value, demands a high degree of accuracy in the fundamental measurements, and it follows that the instrument with which they are made must be precise and finely adjusted, sensitive to slight changes within, and protected from the effects of fluctuations occurring outside of it.

Of fundamental importance in the device is a chamber with walls that are air-tight and heatproof. It must be so large that the subject may live in it in comfort during the time of an experiment, which may continue several hours or several days, and yet not so large that its volume

will prevent the accurate measurement of the amounts of the different gases in the air inclosed. Its walls must be absolutely air-tight, because any leakage of air would nullify the determination of the respiratory exchange, and there must be no passage of heat through them, because any transference of unmeasured heat into or out of the chamber would introduce error into the determination of the amount of energy produced within it. In the following pages the construction of the chamber of the apparatus is described, and the auxiliary apparatus and methods employed in determining the respiratory exchange and energy production of a subject in the chamber are explained in detail.

## CONSTRUCTION OF THE RESPIRATION CHAMBER

The respiration chamber is approximately 1.96 meters long, 1.96 meters high, and 1.19 meters wide, the total volume of the empty chamber being close to 4,570 liters. On the side walls are hooks for clothing and shelves for books, food receptacles, and the like. The furniture consists of a chair and a table, and a cot is provided in experiments lasting a day or more. These may be folded into small bulk when not in use, to provide as much space as possible in which the subject may move about, if the nature of the experiment allows freedom of muscular movement. In experiments of several hours' duration, when the subject is to be very quiet, the ordinary chair and the cot are replaced by an adjustable reclining chair in which he may sit or recline at will, the change in position involving almost no effort. When the experiment involves the performance of muscular work, an ergometer of special construction for measuring the amount of muscular work done is included. There is a telephone for communication between the subject inside the chamber and the observer on the outside. Every provision is made for the convenience of the subject within the limits of the experimental conditions. (See Pl. XXXV, fig. 1.)

In one wall of the chamber, facing a window of the laboratory, there is an opening about 48 cm. wide by 54 cm. high, through which the subject enters and leaves the chamber (Pl. XXX). During an experiment this is closed with plate glass sealed in place, and thus serves as a window. On bright days this window will admit sufficient light for reading or writing, but further light is generally provided by a small electric lamp inside, which the subject may locate according to his desire. Near the center of one end of the chamber is a smaller opening through the walls, called the "food aperture," which is closed by a tube having a valve or trap on one end opening into the chamber, and another on the other end opening to the exterior. This comprises an air lock, through which articles such as food receptacles, books, etc., may be passed into or out of the chamber without any interchange of air between the interior and the exterior of the chamber other than that due to displacement by the articles placed in the

aperture. Several small openings in the walls provide for the passage of air pipes, water pipes, and wires for electric current (Pl. XXXII, fig. 1).

The walls, ceiling, and floor of the chamber are of 16-ounce copper, tinned on both sides. Large sheets of copper are used, so that there will be few joints in the walls. The sheets are joined with tightly locked seams heavily soldered, making them air-tight. When the soldering was completed, the tightness of the walls was tested by air pressure, the level of the column of water in a manometer connected with the chamber being observed at frequent intervals for several hours. It remained constant, due allowance being made for the effect of change of temperature or barometric pressure during the test.

The copper-walled chamber is attached to the inside of a framework of structural iron (Pl. XXXI, fig. 2). The sills and ceiling plates are angle iron with legs about 63 by 63 mm., and are bolted together at the corners. The studding for the side walls and the joists for the floor and the ceiling are of light-weight channel iron about 63 mm. wide, bolted to the plates with stiff angles or elbows, with the width of the channel at right angles to the length of the plates (Pl. XXXI, fig. 1.) The chamber is attached to the framework by long, slender stove bolts passed through holes in the edge of the channels and screwed into brass nuts soldered to the outer surface of the copper. Between each channel and the copper attached to it is a strip of wood about 6 mm. thick and 3.5 cm. wide, to prevent actual metallic contact and to interfere with the transference of heat from the copper wall to its iron supporting structure. Between the copper floor and the floor joists is a layer of asbestos lumber about 9 mm. thick (shown in Pl. XXXI, fig. 1), to provide a solid support for the thin metal floor of the chamber.

To the outer edge of the iron structure is attached a surface of sheet zinc corresponding to the copper wall, ceiling, and floor of the chamber (Pl. XXXII, fig. 1). Sheet zinc about the same weight as that of the copper was used. Washers slipped under the heads of the bolts by which the copper wall is attached serve to bind the zinc to the iron. The chamber is thus provided with double metal walls separated by a dead-air space about 7 cm. across, the purpose of which is explained on page 331, in the description of the method of preventing the passage of heat through the walls of the chamber.

The framework of the chamber was made of structural iron, to secure rigidity and to provide a strong support for any apparatus that it might be found advantageous to employ in experiments in which muscular work would be performed. It entails, however, an undue amount of care in making the calorimetric measurements to avoid error that might result because of the heat capacity and thermal conductivity of the iron, as explained on page 338. Should opportunity to reconstruct the apparatus arise, the iron would be replaced by some material that would provide ample rigidity and strength of structure and have less thermal capacity and conductivity.

The chamber does not rest upon the floor of the laboratory, but is supported about 45 cm. above it by a structure of channel iron (Pl. XXXII, fig. 1), with upright pieces 10 cm. wide, which rest on floor plates and are bolted to the ceiling and between which are cross pieces 7.5 cm. wide, on the lower of which rests the chamber. To this structure is also attached the framework for supporting an outer covering of cork board, described on page 334. This covering is constructed so that it may be easily detached to provide ready access to any part of the zinc wall. The outer surface of the cork board is covered with a layer of museum board 6 mm. thick, painted white on the outside (Pl. XXX).

## DETERMINATION OF RESPIRATORY EXCHANGE IN THE CHAMBER

The atmosphere of the empty chamber contains oxygen, nitrogen, water vapor, and carbon dioxid in proportions like those of ordinary air. When the subject enters the chamber, the proportions begin to change, with the consumption of oxygen and the elimination of water vapor and carbon dioxid. The removal of the water vapor and carbon dioxid from the air and the restoration of oxygen to it in such manner that the quantity of each may be accurately measured form the basis of the determination of the respiratory exchange in the chamber.

The respiratory products are constantly carried out of the chamber by a current of air that is kept in circulation through the system. The air leaves the chamber in a pipe which opens near the floor at one end, passes through purifying devices, and returns to the chamber in a pipe which opens near the ceiling at the other end. The purifying devices, called "absorbers," remove from the air passing through them the water vapor and carbon dioxid imparted to it by the subject. The increase in the weights of the absorbers in a given period shows the quantities of water vapor and carbon dioxid carried out of the chamber during the period. In addition to the data thus obtained, account must be taken of changes in the quantities of water vapor and carbon dioxid in the air of the chamber, as shown by analyses of samples of the air at the beginning and the end of the period, in determining the quantities produced in the chamber during the period (p. 310).

Oxygen is supplied to the chamber from a cylinder of the gas under pressure, and the loss in weight of the cylinder shows the quantity admitted during the period. To determine from data thus obtained the quantity of oxygen consumed by the subject, allowance must be made for changes in the quantity of oxygen in the air of the chamber.

## AIR-TENSION EQUALIZER

The volume of air in the chamber varies constantly with the admission of oxygen and the removal of water vapor and carbon dioxid, and also with changes in the temperature of the air in the chamber and in the barometric pressure of that outside. This might result in undesirable

variations in the pressure of the air in the chamber unless provision were made for corresponding fluctuations in the capacity of the system. This is accomplished by attaching a flexible diaphragm of thin rubber or a sensitive spirometer to a small tube opening into the chamber, which serves as a tension equalizer, keeping the air of the chamber always at the barometric pressure of that of the laboratory (Pl. XXX).

### AIR-PURIFYING SYSTEM

The circulation of air is maintained by a rotary air pump, which has a capacity of close to one-fourth of a liter per revolution and is driven at a rate of about 250 revolutions per minute, so that the air is forced through the purifying system at a rate of 60 to 70 liters per minute. An electric motor of one-eighth horsepower is sufficient to run the pump and to move the air through the absorbers (Pl. XXXII, fig. 2).

All piping in the air-circulating system is brass pipe of the so-called half-inch size, which has an internal diameter of 15 mm. The apertures of the air passages in the purifying devices are also of this size. This has been found sufficient to conduct the air at the desired rate without undue resistance, the pressure in the section of pipe between the compressor and the first water absorber, where it is higher than in any other part of the system, being less than 40 mm. of mercury.

The motor, the rotary air pump, and the absorbers for water vapor and carbon dioxid are assembled on a suitable-sized stand or table, with three shelves, called the "absorber table" (Pl. XXXIV, fig. 1). The motor and pump are on the lower shelf, and on the middle shelf are the purifying devices in a series or train; first, the absorbers for water vapor, and next, the absorbers for carbon dioxid. The air pipe from the respiration chamber passes to the pump and then to the inlet end of the absorber train. From the outlet end of the train the air pipe returns to the chamber, the ingoing and outgoing pipe passing through the walls in two apertures close together. Inside the walls the pipes extend to opposite ends of the chamber, the end of the ingoing pipe being near the top of the chamber, and that of the outgoing pipe near the bottom.

Two absorber trains are set up in parallel and are used in alternate periods, the air pipe at each end of the trains being branched for this purpose. There is a valve in the piping at each end of each train, and the change from one train to the other involves merely closing the valves for one train and opening those for the other. When ordinary wheel valves are used, as shown in the illustration, the motor is stopped for the few seconds necessary to make the change; but the valves at each end of the purifying system may be replaced by a suitable 3-way cock or air trap at the point where the air line branches at each end of the train, and the two cocks may be actuated by the same shaft, so that the air current can be shunted from one train to the other with a single motion from either end of the absorber table and while the air pump is

still running. By actuating the shaft electrically the change can be made by the observer at a distance, or a clock can be used to close the electric circuit at any given time and thus make the change automatically.

While the air is passing through one train the other is disconnected, the absorbers weighed, the absorbent renewed if necessary, and the train again connected in position. The absorbers are joined together by couplings which are attached to the inlet and outlet tubes by stout, flexible rubber tubing. Rubber washers between the halves of each coupling make a tight joint. A similar coupling connects each end of the train with the air pipe. When the whole train is in position it is tested for tightness, with the air in the system at a pressure of about 1 meter of water, which is considerably more than the highest pressure in any part of the train in service.

### Removing Water Vapor from the Air

In the purifying system the air passes first through sulphuric acid, which removes all water vapor from it. The acid container, which is in effect a modified gas-washing bottle of moderately large capacity (Pl. XXXIII, fig. 1), was devised in connection with these investigations. A strong glass bottle about 2½ liters in capacity (about 24 cm. in height and 12 cm. in diameter), with a wide mouth, is fitted with a special ground-glass stopper, in the top of which are sealed an entrance and an exit tube, each 15 mm. in internal diameter. The entrance tube, which is in the middle of the stopper, extends to very near the bottom of the bottle, and terminates in a bulb about 4.5 cm. in diameter, which has several holes about 4 mm. in diameter in the sides and bottom, the total area of the holes being about equal to that of the cross section of the tube. Surrounding the bulb is a bell of about 7.5 cm. diameter, attached to the tube at a point a little above that at which the bulb is attached. The bell is completely open at the bottom, and has a row of holes about 7 mm. in diameter around the side at a level just above the top of the bulb.

When charged, the bottle is filled with acid to a level a little above the row of holes in the bell, about 750 c. c. of acid being sufficient for this purpose. The air escaping through the holes in the bulb and in the bell is broken into bubbles, which in passing through the acid are deprived of moisture. The passage of the air through the acid keeps it vigorously stirred, acid coming up through the bottom of the bell to replace that forced out through the holes at the sides. To prevent globules of acid from being spattered or carried by the air into the exit tube, the bottom of the stopper, which is about 6 cm. below the top, is nearly closed, an annular space about 8 mm. across being left around the tube that projects to the bottom of the bottle to provide for the exit of air. Into the space thus formed in the interior of the stopper are placed lumps of

pumice stone, which effectually prevent visible particles of acid from being spattered into the exit tube or carried into it by the air current.

During several years' use these bottles have proved to be very satisfactory. Before they were used in experiments a large number of tests of their efficiency were made, in which air was passed at various rates up to 80 liters per minute through three of the bottles in series, the first one containing water, in which the air became very moist, and the other two charged with acid. It was found that the moist air leaving the first bottle could be passed through the acid in the second bottle until it was diluted to nearly twice its bulk before the third bottle increased appreciably in weight. No gain in weight was ever observed in a third acid bottle included in the series in some of the tests. In many of these tests the water vapor in the air leaving the water bottle was very nearly saturated at the temperature of the laboratory. These conditions imposed as severe a test on the capacity of the device to remove all moisture from the air flowing through it as any that would occur in respiration experiments.

In practice, two bottles are used in series and the first one is recharged when the acid in it has become diluted to a volume indicated by a mark on the bottle, in which case 750 c. c. of acid have usually absorbed 500 to 600 c. c. of water. Each bottle with its charge of acid weighs not far from 2,600 gm. The two acid bottles will stand side by side on the pan of the large sensitive balance, and are weighed together to an accuracy of 0.1 gm. The increase in the weight of these two absorbers in a given period shows how much water vapor has been carried out of the chamber during the period.

### Removing Carbon Dioxid from the Air

The air from the acid bottles passes next through bottles containing soda lime (a mixture of caustic soda and quicklime), which deprives it of carbon dioxid. The soda-lime container that has been in use for several years consists of an ordinary wide-mouth bottle about 25 cm. in height and 13 cm. in diameter. The mouth of the bottle is closed with a No. 12 rubber stopper, through which pass an inlet tube and an outlet tube of brass pipe, with a bore of 15 mm. The inlet tube extends nearly to the bottom of the bottle. The lower opening of this tube is protected with brass wire gauze to prevent particles of soda lime from entering it. The outlet tube extends outward from the under side of the stopper. When the stopper is tightly sealed and bound in place, soda lime in particles about the size of a dried pea or smaller is introduced through the outlet tube until the bottle is filled quite near to the top. Each bottle when thus charged contains a little over 2 kgm. of soda lime and weighs about 4 kgm.

Two of these bottles are used in series, and each one is kept in use until the appearance of the soda lime indicates that it is no longer effi-

cient enough for further use, which is shown by its change in color. The fresh, somewhat moist soda lime is a dingy white, but in use it becomes much lighter and clearer, owing to both the absorption of carbon dioxid and the loss of moisture, which is taken from the soda lime by the dry air. The bottle may be recharged whenever all of the visible surface of soda lime has thus changed, though if the whitened material has not become compacted into a hard mass which will prevent air from passing through it the efficiency of the soda lime may be restored by passing air containing water vapor through the bottle until the dry material has absorbed about as much moisture as it contained originally, as may be judged from the darkening of the color. In this manner a given charge may be used at least twice. In either case, if the bottle is opened, any soda lime not compacted but still remaining granular may be used again, especially if it is mixed with a large proportion of fresh material. In an ordinary rest experiment in which carbon dioxid is removed from the air current at a rate of 25 to 30 gm. an hour, the material in one of these bottles will absorb at least 150 to 200 gm. of carbon dioxid before all the soda lime has whitened.

These bottles are quite satisfactory in many respects, but in using them great care is necessary to avoid leakage of air between the stopper and the neck of the bottle, or between the stopper and the tubes passing through it, especially after the bottle has been in use a short time. When these joints are made, they are thoroughly painted with shellac, but since the stopper is quite flexible there is possibility of breaking the coating in using the bottle. Some of these chances for leakage will be eliminated by a special cover designed to be clamped to the top of the bottle, into which the inlet and outlet tubes are soldered.

The soda lime is used moist rather than dry because it is more efficient in that condition. In passing through this moist material the dry air from the water-vapor absorber takes moisture from it. The air from the carbon-dioxid absorber is therefore passed through another bottle of sulphuric acid, to catch the moisture given off by the soda lime. This bottle is weighed with the two soda-lime bottles to find the amount of carbon dioxid removed from the air current coming from the respiration chamber, the three bottles standing together on the pan of the large balance being weighed as a unit. Their total weight, which is less than 12 kgm., is ascertained accurately to 0.1 gm.

### Trap for Atomized Sulphuric Acid

Though the pumice in the stopper of the sulphuric-acid bottle effectively arrests visible particles spattered up by the vigorous agitation of the acid or blown up in the air current, acid in some condition, apparently resembling vaporous exhalation, escapes in the air leaving the bottle. The amount of acid that leaves the absorber is so small that even after the air

has been passing for several hours the loss has no effect on the weight of the absorber within the limits to which the weight is determined; yet if the acid carried in this manner from the bottle mentioned in the preceding paragraph is allowed to escape into the air of the chamber, it has a noticeable effect upon the respiration of the subject in a few minutes. To avoid this effect, the air from the absorber passes through a trap which removes the acid spray before it enters the pipe for air returning to the chamber. For several years the trap consisted of sodium carbonate between two layers of cotton wool inclosed in a metal cylinder about 15 cm. long and about twice the diameter of the air pipe. Later, a piece of heavy glass tubing was substituted for the metal cylinder (Pl. XXXIV, fig. 1), and it was observed that the air was freed from acid apparently by mechanical filtering rather than by chemical action between the acid and the carbonate. The first layer of cotton arrested all the acid that reached the trap during several months' use, and the carbonate appeared to be unnecessary. In accordance with this suppositoin, the cotton and carbonate in the trap were replaced by pumice stone in pieces very much smaller than those in the stopper of the absorber, and this has prevented the passage of the acid spray into the pipe for ingoing air.

### Supplying Oxygen to the Air

Oxygen to replace that used by the subject is admitted directly to the chamber through a copper pipe of a bore of about 5 mm. passing through an opening in one wall. The supply of oxygen is contained under pressure in a steel cylinder, the outlet of which is closed with a pressure-regulating valve by which the rate of admission of oxygen is governed. No attempt is made to keep any definite proportion of oxygen in the air. The regulator valve is usually set to admit oxygen at a rate that will keep the volume of gas in the chamber fairly constant, as indicated by the rubber diaphragm or the spirometer serving as an air-tension equalizer for the chamber. The valve may be opened or closed by hand as regulation of the volume is necessary; or by causing the diaphragm or spirometer when nearly full to open and when nearly empty to close an electric circuit, an auxiliary valve may be operated so that the admission of oxygen is automatically regulated to keep the total volume of air in the chamber within the desired limits. A simple auxiliary valve consists of a pinch-cock actuated by an electromagnet so as to compress or release the rubber tubing connecting the outlet of the regulating valve with the end of the pipe taking oxygen to the chamber.

The steel cylinder containing the oxygen is suspended from one arm of a large sensitive balance, and from the other arm is suspended a similar cylinder, empty, to serve as a counterpoise (Pl. XXXIV, fig. 1). The loss in weight of the charged cylinder in a given period shows the amount of gas admitted to the chamber during the period. Though each cylinder

weighs nearly 60 kgm., the loss in weight is ascertained to an accuracy of 0.1 gm.—that is, the volume of gas supplied, which may reach 80 liters or more per hour, may be determined within 100 c. c.

This method of determining the quantity of gas admitted to the chamber is very precise, but it involves time and effort that could be saved by the use of a gas meter if the mere reading of the dial of the meter would show the quantity with equal precision. In a number of experiments the gas from the weighed cylinder was passed through a calibrated test meter before it entered the chamber, to determine whether the volume of gas admitted could be ascertained in this manner with sufficient accuracy. It was found that when the gas was admitted at a fairly uniform rate throughout the period, the volume as determined from the meter reading would agree quite closely with that computed from the loss in weight of the cylinder; but when it was necessary at times to admit gas rapidly, the agreement was not so close, a correction being necessary for increase of pressure in the meter. The time and labor involved in reading, recording, and correcting for increased pressure in the meter are at least as much as those of weighing the cylinder.

In most of the investigations with this respiration calorimeter the gas contained in the cylinder, and consequently that admitted to the chamber, was about 97 per cent oxygen. It was derived from liquid air and was virtually free from carbon dioxid and water, but contained a small proportion (about 0.3 per cent) of nitrogen and an appreciable proportion (about 2.7 per cent) of argon, for which allowance must be made in computing from the loss in weight of the cylinder the quantity of oxygen admitted to the chamber. In making the correction it is sufficiently accurate to consider the impurity as all argon. It is possible, however, to obtain oxygen that is so nearly free from other gases that the error involved in disregarding them is inconsiderable.

### DETERMINATIONS OF THE AMOUNTS OF RESIDUAL GASES

As has been stated (p. 304), to determine the amount of oxygen consumed and of carbon dioxid and water vapor produced by the subject in the chamber during a given period, allowance must be made for any changes that have occurred in the composition of the air of the chamber—that is, in the quantities of different gases residual in the chamber. These are ascertained from analyses of samples taken at the beginning and the end of the period. Because of convenience, the samples are taken, not directly from the air of the chamber but from that passing through the air pipes outside of the chamber. It is assumed that the air in the outgoing pipe has the same composition as that in the respiration chamber. Though the composition of the latter is constantly changing, an electric fan keeps the total mass of air in the chamber energetically stirred to prevent stratification and to mix the varying component gases as thoroughly as possible. It seems probable, there-

fore, that the composition of the air in the outgoing pipe fluctuates quite uniformly with that of the total air in the chamber.

### Analysis of Sample for Water Vapor and Carbon Dioxid

For the determination of the amounts of moisture and carbon dioxid residual in the chamber at the end of each period, a portion of the air coming from the chamber at that time is shunted from the main current through a petcock in the air pipe at a point between the rotary pump and the first sulphuric-acid bottle, and is passed first through a small purifying system and then through an accurate gas meter, which rests on the top shelf of the table for the large absorbers, as seen in Plate XXXVI, figure 2. The air leaving the meter is passed through sulphuric acid to remove the water vapor taken up by it in passing through the meter, and is then returned to the main current flowing from the large absorbers to the chamber. The water-vapor absorbers of the small train are specially devised, somewhat resembling those of the large train, but of such size that they may be weighed on an analytical balance (Pl. XXXIII, fig. 2). A 4-inch U tube with side outlets and well-ground glass stoppers makes a serviceable soda-lime container. A train consisting of one acid bottle, one U tube, and another acid bottle very efficiently removes all water vapor and carbon dioxid from the air passing through it at a rate of about 3 liters per minute.

The small absorbers are weighed on an analytical balance to an accuracy of 0.1 mgm., each unit, when charged, weighing less than 100 gms. The increase in the weights of the units shows the quantities of water vapor and carbon dioxid in a given volume of the air. Usually 10 or 20 liters of air, as indicated by the meter, are passed through the train, the actual volume being ascertained by correcting the meter reading, when necessary, for the calibration of the meter and for the temperature and barometric pressure of the air passing through it.

### Analysis of Sample for Oxygen

For the determination of the proportion of oxygen in the residual air a small sample, about ½ liter, is taken from the returning air in the pipe between the large purifying system and the respiration chamber, where it is free from water vapor and carbon dioxid. In Plate XXXVI, figure 2, a rubber bag for holding the sample is seen hanging from an outlet in the air pipe at the end of the absorber table. A modified Haldane burette is used in the determination, the oxygen being absorbed by a potassium-pyrogallate solution in a Hempel pipette.

### Computation of Volumes of Gases Present

The actual determination of the proportion of oxygen in the air is not necessary at the end of each period. The volume of oxygen present in the air of the chamber may be computed by subtracting from the actual

volume of total air present the sum of the volumes of carbon dioxid and water vapor present, as shown by analyses of the residual air, and the volume of nitrogen, including that present at the beginning of the period and that added with the oxygen admitted during the period, due allowance being made in the latter for any impurity.

To compute the total quantities of carbon dioxid and water vapor in the air of the chamber, the volumes corresponding to the weights of the gases removed by the small absorber system from the air sample measured by the meter are multiplied by a factor representing the ratio between the volume of the sample and the total volume of air in the chamber when both are reduced to standard conditions of temperature (0° C.) and of pressure (760 mm. of mercury). The necessity for accuracy in the analysis of the sample is shown by the fact that under usual experimental conditions there are more than 4,000 liters of air in the chamber; hence, any error in the determination of the quantities of water vapor and carbon dioxid in a 10-liter sample is multiplied over 400 times.

The actual volume of air in the chamber under standard conditions depends upon the capacity of the chamber and the barometric pressure and temperature of the air in it. These factors must be accurately determined, since a difference of 1 mm. in the pressure means a difference of over 5 liters in the computation of the actual volume of gas, while a difference of 1 degree in the temperature means a difference of about 15 liters in the total volume. An error in these determinations has some effect upon the computation of the quantities of residual gases, though the effect of any error likely to occur upon the quantity of water vapor would be quite insignificant, as there are seldom more than 90 liters present, and commonly less. The effect on the computation of carbon dioxid would be somewhat larger, as there might be in some circumstances 100 liters or more in the air; but under ordinary conditions the quantity is decidedly less, and the error would be relatively unimportant. The effect would be greatest upon the computation of the quantity of oxygen, as under normal conditions there could be as much as 850 liters present.

### MEASUREMENT OF CAPACITY OF THE CHAMBER

The capacity of the chamber is known very accurately. It may be computed from the dimensions of the chamber, and it may be directly ascertained by determining the proportion of oxygen in the well-stirred air of the sealed chamber before and after the admission of a known volume of the gas.

### MEASUREMENT OF BAROMETRIC PRESSURE OF THE AIR

The barometric pressure of the air of the chamber, which, because of the air-tension equalizer mentioned on page 304, fluctuates the same as

that of the laboratory, is determined by means of an accurate barometer mounted on the walls of the laboratory. The height of the mercury column in the barometer tube may be read by a vernier to 0.01 mm. The barometer has been standardized by the Weather Bureau.

### MEASUREMENT OF TEMPERATURE OF THE AIR

The temperature of the total mass of air in the chamber is not so easily determined as its pressure. Even when the walls of the chamber are at uniform temperature and no heat is generated in it, the temperature of the air may not be uniform in all parts of the space. When heat is being generated in the chamber and is being absorbed and removed as fast as it is generated, so as to maintain constancy in what is assumed to be the average temperature, there is a considerable difference between the temperature and the consequent density of the air near the source of heat and that of air near the heat absorber. It seems reasonable to suppose, however, that with the tendency of warm air to rise and of cold air to fall, and particularly with the vigorous agitation of the air of the chamber by the electric fan, the warmer and colder volumes of air will be very rapidly mixed, and more or less complete uniformity of temperature quickly established throughout the whole mass of air.

The temperature of the air of the chamber is measured by means of an electric-resistance thermometer. The method of measurement employed is based upon the fact that the resistance of a wire of pure metal to an electric current changes definitely with a change in its temperature and also that the resistance of the wire, and particularly its change in resistance, whether large or small, due to corresponding changes in temperature, may be measured with extreme accuracy by means of a suitable Wheatstone bridge. The device used in the respiration calorimeter comprises specially mounted bare nickel resistance wire in the chamber, connected with a special Wheatstone bridge, called the "temperature indicator," on the observer's table (Pl. XXXVI, fig. 1).

The nickel wire, the resistance of which varies with changes in the temperature of the air of the chamber, is in six coils of equal resistance, each of which is mounted in a rectangular wooden frame about 10 by 13 in. that is suspended in the air about 4 cm. from the wall of the chamber, by supports attached to the wall. The wire is stretched across the space in the frame between two slender wooden rods about 5 cm. apart, with successive strands of the coil about 5 mm. apart. Since very little of the wire is in contact with the support, it is but little, if at all, affected by the temperature of the frame, the object of the construction being to eliminate lag in the action of the thermometer. The exposed wire very rapidly acquires the temperature of the air of the chamber, and hence responds instantly to any changes in it. The six coils are distributed on the walls and ceiling in different vertical and horizontal positions, to

integrate different temperatures if there are differences, and as the air is very thoroughly stirred by the electric fan previously mentioned, it is probable that the resistance thermometer shows the average temperature of the air of the chamber. In the interior view in Plate XXXV, figure 1, two of the frames are plainly shown with a wide-mesh wire screen before the resistance wire to protect it against contact with any object that would cause a short circuit between two parts of the wire, as well as against injury.

The six coils are connected in series by well-insulated No. 16 copper wire, and similar wire leads from the terminals of the series, through a rubber stopper in a small opening in one wall of the chamber, to a special switch on the observer's table, by which they may be connected in one arm of the Wheatstone bridge. The purpose of the switch is to provide means for using with these coils the same bridge that is used with other coils for measuring the temperature of the walls of the chamber and that of the body of the subject, as explained later in this paper. This switch must be designed to avoid the error that would result from introducing appreciable resistance of the switch contacts into the bridge circuits. The connections between the bridge and the resistance coils include a compensating lead to eliminate from the measurement of the resistance of the coils the effect of both the resistance of the leads and any change in their resistance due to change of temperature. The contact that is moved along the slide wire of the bridge, to restore balance when the resistance of the thermometer coils has changed, is in series with the battery, so that contact resistance introduces no error in the measurement.

The six coils have a total resistance of about 20 ohms at 20° C. Since the resistance of nickel wire varies approximately 0.4 per cent per degree at the usual temperatures of the experiments, their total change in resistance would be close to 0.08 ohm for a change of 1° in the temperature of the air of the chamber. The resistance of the slide wire of the Wheatstone bridge will balance the bridge circuit for the change of resistance in the coils that would result from a change of 5° in the temperature. By means of several coils of manganin wire, which may be connected in series with the slide wire, the total range of the bridge may be extended, but under usual experimental conditions the temperature of the air is allowed to change as little as possible. Whether the change is large or small, it must be measured accurately. A change of resistance in the thermometer coils resulting from a change of 0.01° in the temperature of the air will upset the balance of the bridge sufficiently to cause a deflection of the sensitive reflecting D'Arsonval galvanometer that indicates when the bridge is balanced. The balancing point of contact may be moved along the wire a distance sufficiently small to restore the balance, and the scale of the slide wire will indicate the distance.

### OBSERVER'S TABLE

The Wheatstone bridge described above and the telephone mentioned on page 302 are located on the table beside the chamber (Pl. XXXVI, fig. 1) at which the observer sits while controlling the apparatus. The same bridge is employed in the determination of other temperatures, as described beyond. Other devices on the table serve to indicate and regulate temperature conditions inside and outside the chamber, as explained in detail in the sections which follow.

## DETERMINATION OF THE QUANTITY OF HEAT PRODUCED IN THE CHAMBER

Energy expended by the human body for any purpose, such as the performance of muscular work, the maintenance of body temperature, or whatever, results in the production of heat, which is eventually dissipated from the body; hence, the measurement of the quantity of heat dissipated by the body under given conditions affords data for the determination of the quantity of energy expended. Heat escapes from the body in two ways: As latent heat of water vaporized from the lungs and skin and as sensible heat, by conduction, convection, and radiation from the surface of the body to the air and to objects in the chamber. Both latent heat and sensible heat are carried out of the chamber and measured.

### MEASUREMENT OF LATENT HEAT

The water vaporized by the lungs and skin leaves the chamber in the outgoing air, unless it is precipitated by contact with some object in the chamber whose temperature is below the dew point for the conditions prevailing, but the temperature of the air and of objects in the chamber is controlled so that precipitation is not likely to occur. The quantity of heat leaving the chamber as latent heat of water vapor in any given period is determined by multiplying the weight of the water vapor absorbed from the outgoing air during the period by the factor 0.586, which according to determinations made by Smith (18), represents the number of Calories of heat required to vaporize a gram of water at 20° C. All measurements of heat with the calorimeter are expressed in terms of Calories at 20° C., 1 Calorie being taken as the amount of heat required to raise the temperature of 1 kgm. of water 1° C.—i. e., from 19.5° to 20.5°, the specific heat of water being taken as unity at 20° C. The determinations by Smith were made in accordance with the conclusion by Barnes (7) that the mean small calorie is equivalent to 4.1877 international joules. Dickinson, Harper, and Osborne (10), in work on the latent heat of fusion of ice, assumed 4.187 international joules equal to 1 small calorie at 15°, in which case 4.183 joules would be equivalent to 1 small calorie at 20° C. The latter value is used in these investigations (p. 342), but the difference between this and the value by Barnes has no significant effect upon the factor for latent heat here employed.

MEASUREMENT OF SENSIBLE HEAT

The energy eliminated from the body as sensible heat, which is much greater in amount than that latent in water vaporized from the body, is practically all carried out in a current of water which circulates in the chamber through a device called the "heat absorber," though a small quantity of it may become latent in water vaporized from objects in the chamber, in which case it may leave the chamber as latent heat of water vapor in the outgoing air. If the weight of the water that flows through the absorber during a given period, as stated in kilograms, is multiplied by the difference between the temperature of the water as it enters and that as it leaves the absorber, as measured in degrees centigrade, the product will show the quantity of heat removed as expressed in Calories, at the mean temperature of the water flowing in the absorber. These are converted into Calories at 20° by making due allowance for the specific heat of water at the mean temperature of the flow as compared with that at 20° (4, p. 56; 19, p. 229).

The rate at which heat is removed from the chamber is regulated to prevent fluctuations in the temperature of the air of the chamber, which falls when the rate is too fast and rises when it is too slow. To avoid chance for error in the determination of the volume of air in the chamber, which depends upon the accuracy of the measurement of its temperature (p. 313), and to some extent also for the comfort of the subject, it is desirable to keep the temperature of the air as constant as possible. The temperature to be maintained depends upon the nature of the experiment, but it is commonly not far from 20° C. Whatever the requirement may be, by proper control of the temperature at which the water enters the heat absorber, and of the rate at which it passes through the absorber, the removal of heat from the chamber may be made to accord with its production within it to such an extent that the temperature of the air of the chamber may be kept constant within narrow limits. The most convenient practice is to maintain a constant rate of flow and to vary the temperature of the water entering the heat absorber according to the amount of heat to be absorbed.

HEAT ABSORBER

The heat absorber, which is suspended near the ceiling of the chamber, about 10 cm. from the sides, consists of brass pipe of 7 mm. internal diameter (so-called ¼-inch pipe), along which disks of sheet copper 5 cm. in diameter are soldered 3 mm. apart to increase the area of the heat-absorbing surface. The total length of pipe in the absorber is not far from 11 meters, and there are more than 2,500 disks on it, so that several square meters of surface are exposed to the air of the chamber. Though the total quantity of water in the absorber is not over 400 c. c., it is possible, by control of the temperature and rate of flow of the water,

The coil passes once around the chamber and back again, the two pipes lying not quite 5 cm. apart, with the disks on one slightly overlapping those on the other. The purpose of this arrangement is to establish as much uniformity as possible in the absorption of heat from the air enveloping the absorber. Incidentally this would result in corresponding uniformity in the density of the air affected by the absorber.

### Regulating and Measuring the Water Flow

Water for the heat absorber is drawn from a small tank several feet above the ceiling of the chamber, which is filled by water flowing from the city main. An overflow pipe in the tank keeps the water supply at a constant level; and since the level at which the water leaves the absorber is also fixed, the pressure in the system is constant. Under favorable conditions the rate of flow through the absorber is quite regular. At times, however, in cold weather, when a considerable amount of air is dissolved in the water, some of the air that is liberated when the temperature of the water is raised gradually accumulates in the absorber and reduces the rate of flow in an irregular manner. Under these conditions the faster the rate, the more constant it is. For this reason a specially devised rate valve is of only limited service in regulation of the rate of flow, though it has some advantages over the common stopcock.

The water leaving the heat absorber flows into a copper cylinder holding about 3 liters and through a stopcock in the bottom of this into a tank holding about 100 liters. This tank will catch all the water that would leave the heat absorber during a period of at least three hours, in experiments in which the dissipation of heat in the chamber is about 100 Calories per hour, a rate of flow of 350 to 450 c. c. of water per minute, with the temperature of the ingoing water about 16°, having been found quite satisfactory in such circumstances. The large tank rests upon a sensitive platform balance (Pl. XXX) by which the weight of the water is determined to 0.01 kgm. The small cylinder catches the water that flows while the tank is being weighed and emptied.

### Regulating the Temperature of Water Entering the Heat Absorber

The temperature of the water entering the heat absorber is so completely under control that it may be kept indefinitely at any desired point within narrow limits, or may be changed rapidly, if necessary, from one point to another. To accomplish this, the water is first cooled to a temperature below that at which it will be used and then brought to the required temperature by electric heating. In these circumstances, when any change in temperature is desired, it is necessary to vary only the heating. The chilled water passes into a device called the preheater, which does the greater part of the heating necessary to warm the water to the desired temperature. The heating effect of this device is adjusted by hand. From [illegible]

bottle filled with pieces of pumice as large as will pass through the narrow neck. In this reservoir the water is mixed so that any change in the temperature of that entering the bottle, due, for instance, to fluctuations in the voltage of the current in the preheater, will be dissipated through the mass to such extent that there will be no rapid fluctuations in the temperature of the water leaving the bottle. From this reservoir the water enters the final heater which completes the heating necessary to bring the water to the desired temperature. This device functions automatically and varies the amount of heating it does to accord with the fluctuations in temperature of the water coming from the mixing bottle. From the final heater the water flows into a smaller mixing bottle, from which it passes to the heat absorber.

### WATER COOLER

To cool it, the water from the pressure tank is passed through a coil of pipe submerged in cold water, in a tank nearly 1 meter in length by 30 cm. in width and depth and containing 80 to 90 liters of water. The coil consists of nearly 6 meters of iron pipe, of 15 mm. bore, in six parallel rows running from end to end near the bottom of the tank. The water in the tank is chilled by cold brine flowing through a second coil, immersed in the water above the former coil. A small ethyl-chlorid refrigerating machine keeps the temperature of the circulating brine quite uniform. In this manner the temperature of the water leaving the cooling coil is readily kept below that at which it may be needed at any time during an experiment, and fairly uniform, but it can not be regulated by cooling alone as closely as needed for use in the heat absorber.

### WATER HEATER ADJUSTED BY HAND

The preheater consists of several coils of electric-resistance wire of different sizes wound upon a thin-walled brass tube about 16 mm. in diameter, from which they are insulated with mica. Outside of this is a similar tube about 26 mm. in diameter, and the annular space between the two and surrounding the resistance coils is filled with sand, so that the heat generated by the electric current in the resistance wire is transmitted rapidly to both tubes. This heater is mounted inside a brass tube 37 mm. in diameter, in such manner that the chilled water, entering the large brass tube, flows in one direction along the outside of the heater and returns along the inside, absorbing all the heat generated in it. By means of plug switches on the base supporting the heater various combinations of the coils may be put into service, as desired, to vary the heating. By the use of this device the temperature of water flowing at a rate of about 1 liter a minute may be increased nearly 10 degrees, if desired, in increments of about 0.25 of a degree.

There are seven resistance coils in the heater, of which four have a resistance of about 340 ohms each. There would be a little less than 0.65 ampere of current flowing in such a coil at 220 volts, which would give approximately 140 watts. To raise 1 degree the temperature of water flowing at the rate of 1 liter per minute requires approximately 70 watts; hence, each of these four coils would increase the temperature about 2 degrees. The resistances of the three other coils are, respectively, about 680, 1,360, and 2,720 ohms, and their output, respectively, about 70, 35, and 18 watts, with corresponding heating effects sufficient to raise the temperature of the water about 1, 0.5, and 0.25 degree.

If these coils were all wound in one tube, the heater would be inconveniently long. Two similar tubes, each 30 mm. long, are used, with the five coils of smaller resistance in one and the two coils of larger resistance in the other. The cold water flows first through the former and then through the latter. The two tubes mounted side by side on the same base may be seen in Plate XXXVI, figure 2, on a board attached to the side of the calorimeter.

### WATER HEATER OPERATED AUTOMATICALLY

The final regulation of the temperature of the water for the heat absorber is done in a short tube inclosing a water channel, called the "final heater," which is shown in Plate XXXVI, figure 2, beside the preheater, on the board attached to the side of the calorimeter. In the upper end of the channel is an electric resistance thermometer coil that is connected with an indicator on which may be set the temperature at which it is desired to keep the water entering the heat absorber. In the lower end of the channel is an electric heating coil, in series with which is a rheostat for varying the current in the coil. The slider of the rheostat is adjusted by a screw shaft that is driven by a small electric motor. The water passing through the channel flows directly from the heater to the thermometer. If the temperature of the water flowing over the thermometer differs as much as 0.05 degree from that set on the indicator, the armature of the small motor turns in one direction or the other, depending on whether the water is too cold or too warm, and adjusts the rheostat until the current in the coil is just enough to heat the water to the desired temperature.

The water tube in this device, which is 28 cm. long, has a narrow channel, the cross section being 12 mm. in length and 4 mm. in width and having round ends. It was made by flattening thin-walled copper tubing of an external diameter of 1 cm. At each end the tubing is left circular in cross section and is soldered into a short nipple, which is screwed into one end of a special brass fitting with side outlets. Thin-walled brass tubing 2.5 cm. in external diameter, extending from one nipple to the other, forms a case around the channel, protecting it from

mechanical strain and surrounding it by a small dead-air space which serves to some extent as a heat insulator, protecting it from changes in temperature of the laboratory air. The side openings in the fittings provide an inlet and an outlet for the water.

The electric heater, which is in the lower end of the channel, consists of platinum wire, of 55 ohms' resistance, in a flat coil about 10 cm. long and 9 mm. wide, inclosed in a flat case of thin metal which, with the coil inside, is 10 mm. wide and 2 mm. thick. At one end this flat part of the case tapers into a tube about 3.5 cm. in length and 6 mm. in diameter, in which are the wires carrying electric current to the coil. This heater is inserted in the water channel, through the open end of the fitting, to the depth at which the whole of the resistance wire will be immersed in the water current, and a packing device in the end of the fitting is tightened around the neck of the case to hold the heater in place. In the channel the heater is surrounded by a space 1 mm. across, through which the water flows. Heat generated in the coil is imparted instantly to the water which surrounds the heater in such a thin layer that the temperature of the whole mass of water is very quickly affected.

The electric current flowing in the heating coil is determined by ballast resistance in series with the coil, of which 125 ohms are fixed and 550 ohms variable. For the former an ordinary resistance unit is satisfactory, and for the latter a rheostat of oxidized constantan wire of graduated cross section wound on an insulated light-steel tube has given excellent service. The sliding contact on the rheostat may be moved by hand or by means of a screw shaft (Pl. XXXV, fig. 2). When the total resistance of both the rheostat and the resistance unit is in series with the coil, a current of approximately 0.3 ampere will flow in the coil, the heating effect of which is sufficient to increase by a little less than 0.1 degree the temperature of water flowing through the heater at the rate of 1 liter per minute. When the whole of the rheostat is out of the circuit and only the resistance unit is in series with the coil, the current will be approximately 1.2 amperes, with a heating effect sufficient to increase by a little over 1 degree the temperature of 1 liter of water per minute.

Between these limits the heating effect may be varied in large or small steps, according to the distance the sliding contact is moved along the turns of wire in the rheostat. If the position of the slider is adjusted by hand, any portion of the rheostat, from the total resistance to that of a single turn of the wire, may be instantly put into or out of the circuit. That the temperature of the water may be automatically regulated, however, the position of the slider is adjusted by a screw shaft. A small pulley on the end of the shaft is belted to another pulley on the armature shaft of a small electric motor, that may be caused to run in one direction or the other and for a longer or shorter period, depending upon whether the amount of resistance in the circuit must be increased or decreased and how much. The field coils of the motor are differentially

wound, and the direction in which the armature of the motor will rotate depends upon the windings by which the fields are excited. With current flowing in both pairs of field coils alike the armature will not turn in either direction; but if one pair of coils is shunted, the effect of the other pair predominates, and the armature will rotate. The direction of rotation depends upon the closing of one or the other of two contacts in the circuit of the field windings, thereby shunting one or the other pair of field coils, and the duration of rotation depends upon the length of time the contact is closed.

The contacts are closed by keys which are depressed by cams on a light cam shaft driven by a small motor. The cams rotate continuously, and when a circuit is to be closed an idler swings between one of the cams and the key to be depressed. There are three cams for each key, differing in respect to the time each one presses on the idler, and the duration of contact depends upon which of these cams is engaged. Each idler is mounted on a lever which carries it into position between the cam and the key, the lever being actuated by a pin on the rotating shaft. A galvanometer needle decides which lever is to swing and to which of the three cams it is to be carried. The galvanometer, though incorporated in the device for making contacts, is connected with the indicator on which is set the temperature at which the water is to be kept. The direction and amplitude of deflection of the needle depend upon whether and to what extent the temperature of the water is above or below that set on the indicator. The galvanometer thus governs the direction and extent of motion of the slider on the rheostat which regulates the current in the heating coil in the water channel. The period of the galvanometer is less than 3 seconds, and the cam shaft rotates once every 4 seconds, so that changes in the temperature of the water, when necessary, are made that often, giving practically continuous regulation. With three different degrees of automatic adjustment in either direction, and with the possibility of shifting the slider by hand, the water flow may be quickly brought to any desired temperature and easily maintained. This device for causing the movement of the contact on the rheostat is shown in Plate XXXV, figure 2, which shows also the rheostat and the motor for adjusting the rheostat.

The indicator on which the desired temperature is set, which may be seen in Plate XXXVI, figure 2, at the right of the water heaters, is a special Wheatstone bridge, in one arm of which is the resistance thermometer in the water channel. The resistance of the slide wire of this bridge, which is nearly 45 cm. long, is sufficient to compensate for an upsetting of the balance of the bridge due to the change in resistance of the thermometer that would result from a change of 10 degrees in the temperature of the water, and by means of a coil in series with the wire the amount of balance resistance may be doubled. When the coil and slide wire are in series, the range of the dial is from 12 to 24 degrees;

when the coil is not in series, the reading is from 2 to 12 degrees. In each degree there are 10 subdivisions which are about 4 mm. apart, so that it is possible to change the setting of the indicator by as little as 0.05 degree, and the galvanometer connected with the indicator is sensitive to a change of this magnitude in the balance of the bridge. The resistance thermometer which is in one arm of the bridge is a coil of platinum wire, of approximately 25.5 ohms' resistance at 20° C., the resistance of which changes 0.1 ohm with a change of 1 degree in its temperature. The wire is wound in a flat, narrow coil and inclosed in a very thin silver case, resembling that of the heating coil, and similarly mounted in the upper end of the water channel. The resistance wire very rapidly acquires the temperature of the water flowing in the millimeter space surrounding the case, and changes in resistance instantly follow very small changes in the temperature. The thermometer is a short distance from the bridge, as shown in Plate XXXVI, figure 2, and connected with it by leads that are compensated so that the effect of the resistance of the leads and of change in their resistance due to change in temperature is eliminated.

From the final heater the water flows into a bottle of about 1-liter capacity, nearly full of broken pumice, and then into the heat absorber.

### Measuring the Temperature Increase in Heat Absorber

The water that has passed through the heat absorber will have increased in temperature according to its rate of flow and the rate of production of heat in the chamber. The accuracy with which the increase in temperature is determined is of fundamental importance in the measurement of heat generated.

#### Measurement by mercury thermometers

The difference between the temperature of the ingoing and that of the outgoing water was formerly determined by reading two mercury thermometers installed in the water circuit, with the bulb of one in the water just entering the chamber and the bulb of the other in the water just leaving it. The thermometers were as sensitive as it was practicable to employ and were very accurately calibrated. Each had a range of about 12 degrees, with graduations of 0.02 degree, the one in the ingoing water reading from 0° to 12° and the one in the outgoing from 8° to 20°, and by judging the position of the mercury between the graduations the temperature was estimated to 0.01 degree. The observer read the thermometers and recorded the temperatures every two or four minutes, which, in addition to the other duties at the observer's table, was rather tedious and trying. Both thermometers were supposed to be read simultaneously, but as this was impracticable for one observer the two thermometers were read as quickly as possible, and then the

observations were recorded. This method afforded opportunity for errors in fundamental data, some of which might be obvious, but most of which would not be detected.

MEASUREMENT BY ELECTRIC-RESISTANCE THERMOMETERS

To relieve the observer of the tedium of these observations, and especially to eliminate as much as possible of the personal element from the measurement, the mercury thermometers were replaced by a device for measuring the increase in the temperature of the water by the difference in electrical resistance of two coils of wire in the water circuit. Atwater and Rosa (4, p. 25; 5, p. 151) employed a device of this character in their original calorimeter, but did not develop it to measure temperature differences with the same degree of accuracy as the one here described. The latter device comprised two special resistance coils, a special Kohlrausch bridge, a sensitive galvanometer, and a lamp and scale for reading the deflections of the galvanometer. The specially mounted resistance coils, called the "bulbs," were inserted in the water line where the bulbs of the mercury thermometers had been and were connected with the special Kohlrausch bridge on the observer's table, the two coils being in opposite branches of the bridge circuit, with the slide wire between them. The reflecting D'Arsonval galvanometer by which the bridge was shown to be balanced was suspended in such a position that the scale on which the deflections of the galvanometer were read was on a level with and directly in front of the eyes of the observer sitting at the table. The movement of the galvanometer was indicated by the movement of a vertical line of light along the scale, the light from a straight-filament electric lamp being reflected by the mirror of the galvanometer. To determine the difference in the temperature of the two coils, it was merely necessary to move the battery circuit contact along the slide wire of the bridge until the line of light was at the center of the scale, showing that the bridge was balanced. The reading of the bridge scale was then recorded. To balance the bridge and read its scale was much more convenient than to read the mercury thermometers, and only one record was involved.

Several types of resistance-thermometer bulb were tried in connection with this device. In one, insulated resistance wire was incased in a coil of small-bore lead tube, which was immersed in an enlargement in the water channel. This proved unsatisfactory for several reasons. One was that it did not respond quickly enough to changes in the temperature of the water, owing probably to poor thermal contact between the wire and the tube; and the mass of metal in the tube also tended to increase the lag. Another was that the space in the lead tube was not deprived of water vapor, and this eventually moistened the insulation of the resistance wire, so that a short circuit was established between the wire and the

tube sufficient to ruin the bulb for accurate measurement of temperature. After the bulbs had been in use a short time they would produce an electromotive force as if they were primary or secondary cells.

In another type of thermometer bulb the resistance wire was inclosed in a thin-walled small-bore copper tube, which was filled with Wood's metal to exclude moisture from the tube and to render the thermometer more sensitive by increasing the conduction of heat to the wire. This bulb did not prove satisfactory because, though the thermal conductance from the water to the wire may have been improved, the sensitiveness of the thermometer was not, the mass of metal apparently causing a lag in response to temperature change. Furthermore, the Wood's metal apparently did not completely exclude moisture, for ultimately the wire in this thermometer also became short-circuited with the metal. Another serious objection was the possibility that the resistance wire might be stretched by the unequal expansion of the metal in which it was embedded.

The bulb which was finally used with utmost satisfaction was constructed in accordance with the specifications of the one developed by Dickinson and Mueller (11, 12, 13) in connection with investigations on calorimetry at the United States Bureau of Standards, which was designed especially for use in determining the temperature at a definite point of liquid flowing in a tube in a continuous-flow calorimeter. The bulbs were designed especially to combine constancy, freedom from lag, and intimate contact with the entire water flow. The platinum resistance wire was wound on a thin strip of mica, and this coil, laid between two similar mica strips, was inclosed in a flat sheath of thin silver which pressed the mica insulating strips firmly against the resistance wire, thus affording opportunity for rapid conduction of heat between the case and the wire. The silver case terminated at the top in a tube which was sealed to a glass tube, on the end of which was a bulb containing phosphorus pentoxid, the purpose of which was to exclude moisture from the space in which the resistance wire was inclosed. The flat part of this bulb, which was about 10 cm. long, 10 mm. wide, and 1 mm. thick, and contained the sensitive part of the thermometer, was inserted in a brass tube with a constricted channel, like that for the final heater described on page 319, so that the sensitive portion of the thermometer was surrounded by a space about 1 mm. across; and water flowing through this space was thus brought into intimate contact with the thermometer, which very rapidly acquired the temperature of the water and responded instantly to changes in temperature and integrated stream lines of temperature, if any existed. The two thermometers, one in the ingoing and the other in the outgoing water, had exactly the same resistance, about 25.5 ohms at 20° C., and the same coefficient of change of resistance with change in temperature, about 0.0039 per degree for the range of temperature in which they would be used, the resistance change of each thermometer being 0.1 ohm per

degree. With the regular leads to each thermometer from one branch of the bridge circuit was a compensating loop from the opposite branch of the bridge, to balance the resistance of the leads in both branches of the circuit, and to eliminate the effects of changes in the resistance of the leads due to changes in their temperature and of thermal electromotive forces. All connections in the bridge circuit were soldered—that is, there were no contact connections; hence, no possibility of error due to contact resistance in any part of the circuit.

The special Kohlrausch bridge was designed to measure any difference as large as 10 degrees or as small as 0.01 degree in the temperature of the water as it entered and as it left the heat absorber. The slide wire of the bridge, which was about 4.5 meters long, consisted of 10 turns of manganin wire wound spirally on a cylinder of marble about 15 cm. in diameter. The battery-circuit contact, which balanced the bridge by the adjustment of its position on the slide wire, was mounted on the inside of a hood surrounding the cylinder, which, when rotated, moved up or down on a threaded center post. Since the contact was in the battery circuit, whatever contact resistance there might be had no effect on the balancing point of the bridge. The resistance of the total calibrated portion of the slide wire was sufficient to balance the bridge when the resistance of the two thermometer coils differed by as much as 1 ohm, which would occur with a difference of 10 degrees between the temperature of the ingoing and that of the outgoing water. With one rotation of the hood the contact was moved over sufficient of the slide wire to balance a difference of 0.1 ohm or 1 degree in the thermometers. On the edge of the hood was a scale with 200 divisions, each corresponding to a little over 2 mm. of the slide wire. A movement of the contact on the wire the space of two divisions would be sufficient to balance a difference of 0.001 ohm or 0.01 degree in the thermometers.

The sensitivity of the galvanometer was sufficient to indicate a change of even one division in the bridge setting, equivalent to 0.005 degree in the temperature of the thermometer. With the usual current of 0.03 ampere in each half of the bridge, a change of 0.001 ohm would be indicated by a deflection of several millimeters on the galvanometer scale. A current of 0.03 ampere flowing in each resistance thermometer would not cause an increase of 0.005 degree in the temperature of either, when immersed in water flowing at the rate of 200 c. c. per minute, which would be not over half the common rate in the experiments.

Provision was made for checking the results obtained with the electric-resistance thermometers. The second type of resistance bulb mentioned above was constructed so that the bulb of the mercury thermometer formerly used could be inserted into the bulb of the resistance thermometer, and the temperature differences determined by both sorts of thermometers at the same time. The results obtained by the two

methods before the resistance coils became short-circuited were always in very satisfactory agreement, but this was hardly a sufficient test of the accuracy of the resistance method, because the measurement of temperature difference by the electric-resistance thermometers is much superior to that by the mercury thermometers in sensitivity and precision. With the third type of resistance bulb a more satisfactory method of checking was provided. A differential thermoelement, with several junctions of copper and constantan wire in each end inclosed in thin glass tubing, was mounted with one end in the water just leaving the ingoing thermometer and the other end in the water just entering the outgoing thermometer. The terminals of the thermoelement were connected with binding posts on the observer's table, from which connection could be made with a potentiometer, by means of which temperature differences could easily be measured to an accuracy of 0.01 degree. Measurement of the increase in temperature of the water flowing in the heat absorber by means of this apparatus afforded a real check on the measurement with the resistance thermometer.

### MEASUREMENT BY TEMPERATURE DIFFERENCE RECORDER

As a matter of fact, this method of measurement could be employed instead of the resistance-thermometer method when the readings are to be made and recorded by the observer. Either method was more convenient and decidedly more sensitive than the mercury thermometers, and by use of it the temperature difference was actually measured to 0.01 degree, whereas in reading the mercury thermometers the temperature was only estimated to 0.01 degree. The particular advantage in the resistance thermometers was in the opportunity to use with them a device which gives automatically a practically continuous record of the difference between the temperature of the water entering and that of the water leaving the heat absorber. A device of this character which has been employed for five years in the investigations with the present respiration calorimeter has proved very satisfactory indeed and relieves the observer of a considerable amount of drudgery, while it entirely eliminates the possibility of error due to personal inaccuracy in recording data regarding the temperature differences.

Like the resistance thermometers described above, the two coils used in this device have the same resistance, approximately 25.5 ohms, at the same temperature, and the same change in resistance with the same change of temperature, but the bulbs differ somewhat in mechanical construction from the earlier type. The platinum resistance wire is not in a thin, flat coil in a flat sheath, but is in a helical coil in a narrow annular space between two metal tubes with thin walls. The wire is wound upon the inner tube, and the outer tube fits close against it, an electrical insulation of thin sheet mica separating the wire from each tube. The space between

the tubes is tightly closed at each end, the leads from the resistance wire being carried out through a small tube attached to the tube surrounding the wire. As in the flat-type thermometer, this small tube terminates in a bulb containing phosphorus pentoxid, to keep the annular space free from moisture. The cylindrical shell inclosing the resistance wire is mounted in a brass tube which provides a water channel so designed that the water flowing in it passes inside the inner and outside the outer of the tubes incasing the wire, which is thus brought into intimate contact with all the water flowing through the thermometer, and responds instantly and accurately to changes in its temperature. Because of the design of the thermometer and the manner in which it is mounted in the walls of the chamber, the usual fluctuations of the temperature of the air adjacent to the case of the thermometer introduce no error in the measurement of the temperature of the water flowing in the bulb. One of these thermometers is placed in the incoming water pipe so that it will be at the temperature of the water just as it passes through the copper wall, and the other is similarly placed in the outgoing water pipe.

The two thermometer coils are in the corresponding arms in opposite branches of the circuit of a special Wheatstone bridge (Pl. XXXV, fig. 2), which may be accurately balanced for inequalities in resistance of the coils as small as 0.001 ohm and as large as 1 ohm, resulting from a difference of 0.01 degree and of 10 degrees, respectively, between the temperature of the water entering and that of the water leaving the heat absorber. The total resistance of the slide wire of the bridge will compensate for an inequality of 0.2 ohm in the resistance of the coils which results from a difference of 2 degrees in their temperature. If there is no difference in the temperature of the water in the two thermometers, the bridge is balanced with the battery circuit contact at the low end of the wire, while if the temperature of the water leaving the heat absorber is 2 degrees higher than that of the water entering it, the bridge is balanced when the contact is at the upper end of the wire. To compensate for inequalities due to temperature differences greater than 2 degrees, eight coils of manganin wire in series are arranged so that any number of them may be connected in series with the slide wire, thus shifting the position of the contact on the wire at which the bridge may be balanced and altering the significance of the balance point in temperature difference. The lower end of the wire may thus be made to correspond to any whole number of degrees of temperature difference between 0 and 8, with the upper end 2 degrees higher in each case. The coil and slide wire are joined by means of a heavy copper link, with one end in the mercury cup in which one end of the slide wire terminates and the other end in a similar cup in which an end of the extension coil terminates.

The slide wire of the bridge is incorporated in a mechanism (Pl. XXXV, fig. 2) which automatically balances the bridge for inequalities of resist-

ance in the thermometer coils and records the balancing operations in terms of temperature difference and time. The wire is mounted in a bar which supports and guides a slider carrying the battery circuit contact point along the slide wire. The slider is actuated by a small electric motor, the direction and extent of motion of the slider being governed by the direction and the amplitude of deflection of the pointer of a galvanometer which is connected between the two branches of the bridge circuit, and is incorporated with the slide wire in the mechanism which balances the bridge. The direction in which the pointer will swing depends upon whether the inequality of resistance of the thermometer coils increases or decreases—that is, whether the difference between the temperatures of the water in the thermometers grows larger or smaller. For example, if the temperature of the outgoing water rises or that of the ingoing water falls, the pointer will swing so as to cause the slider to move toward the high end of the wire. The amplitude of deflection of the pointer depends upon the magnitude of the inequality of resistance of the thermometer coils. The bridge and galvanometer are sensitive to very small temperature changes in the thermometer. With the measuring current of 0.05 ampere in each thermometer coil a difference of 0.0005 ohm in the resistance of the two coils, which results from a difference of 0.005 degree in the temperature of the water in the thermometer, causes a deflection of the pointer sufficient to influence the position of the contact on the slide wire. With a measuring current of 0.05 ampere each coil would dissipate about 0.06 watt, which would be sufficient to raise the temperature of the thermometer 0.005 degree if the water were flowing through it at a rate of only 200 c. c. per minute; but since the rate of flow is generally twice as great, the effect of the measuring current on the temperature of the bulb is negligible.

Each time it changes the position of the battery circuit contact point on the slide wire the automatic shifting mechanism moves the slider one of three different distances in either direction, according to the amplitude of deflection of the galvanometer pointer. With the smallest change of position the contact is moved along the wire sufficiently to balance the bridge for inequality of resistance in the thermometers due to differences of less than 0.01 degree in the temperature of the water. The medium change balances differences of resistance equivalent to differences of nearly 0.03 degree in temperature, and the large change corresponds to temperature differences of 0.05 degree. The shifting mechanism functions every 7 seconds; hence, it will keep the bridge in balance for any change in temperature difference not exceeding 0.4 degree per minute; but inasmuch as the position of the contact point on the slide wire may be easily adjusted by hand for any inequality of resistance within the range of the instrument, any alteration in temperature difference may be followed.

As the slider moves back and forth on the bar which supports the slide wire, it carries a pen which draws a curve on ruled paper by which the movement of the contact point on the slide wire is expressed in temperature. The total width of the paper scale, 25 cm., represents a difference of 2 degrees between the temperature of the water entering and that of the water leaving the heat absorbers, and corresponds exactly to the length of the slide wire by which the bridge is balanced for the inequality of resistance in the thermometer coils resulting from such a temperature difference. The temperature difference indicated by the position of the pen on the paper scale coincides with that to which the position of the contact point on the slide wire is equivalent. The paper scale is ruled with 100 lines, each representing 0.02 degree, and as the distance between the lines is 2.5 mm., the curve may easily be interpreted to 0.01 degree. The paper is moved forward at a very regular rate, approximately 7.5 cm. per hour, by the motor which moves the slider, the speed of the motor being regulated by a governor so that it is uniform, even with wide fluctuations in voltage of the current by which the motor is driven. Since the necessary changes in the position of the slider are made every 7 seconds, the curve gives a practically continuous record of the temperature difference.

The difference between the temperature of the water as it enters and that as it leaves the heat absorber may thus be easily read at any instant to 0.01 degree. The accuracy of the measurement of temperature difference by the apparatus may be tested at any time, even during the course of an experiment, without interfering with the record, and such tests are made at frequent intervals. In the water channel in the center of each resistance-thermometer bulb is the end of a differential thermoelement of 0.125 mm. copper and constantan wires, having 11 junctions in each end, inclosed in 4-mm. glass tubing, with thin wall. The element remains permanently in position, though it may be easily removed if necessary. The terminals of the element are joined by insulated 1-mm. copper wire to binding posts on the observer's table, from which connection can be made with a potentiometer whenever a test is to be made. With this differential thermoelement, which has been calibrated over a wide range of temperature at the United States Bureau of Standards, an electromotive force of over 4.5 microvolts results from a difference of 0.01 degree in the temperatures of the two ends. By means of the potentiometer and galvanometer with which it is employed, an electromotive force of half that magnitude is easily measured; consequently temperature differences may be measured by it to an accuracy at least as good as 0.01 degree. Measurements made with this apparatus therefore serve to indicate the accuracy of those with the recorder. The agreement of results obtained by the two methods of measuring the increase in the temperature of the water flowing through the heat ab-

sorber is shown in Table I, which summarizes data obtained in an alcohol check test (see p. 342) of the calorimeter made in January, 1915, which continued for two consecutive periods of three hours each.

TABLE I.—*Comparison of data for heat measurement obtained by use of temperature difference recorder and of thermoelement with potentiometer*

| Time. | Water flow. | Temperature difference. | | Heat computed from measurement. | |
|---|---|---|---|---|---|
| | | By recorder. | By potentiometer. | By recorder. | By potentiometer. |
| | *Kgm.* | *Degrees.* | *Degrees.* | *Calories.* | *Calories.* |
| 1 hour | 20.53 | 3.99 | 4.01 | 81.9 | 82.3 |
| Do | 21.20 | 3.97 | 3.96 | 84.2 | 84.0 |
| Do | 23.00 | 3.73 | 3.73 | 86.0 | 86.0 |
| Total | | | | 252.1 | 252.3 |
| 1 hour | 23.00 | 3.68 | 3.68 | 84.6 | 84.6 |
| Do | 23.21 | 3.57 | 3.54 | 82.9 | 82.2 |
| Do | 22.72 | 3.67 | 3.67 | 83.4 | 83.4 |
| Total | | | | 250.9 | 250.2 |

In order that the recording device may continue to measure temperature differences with the accuracy required, not only must the bridge be sensitive to a change as small as 0.002 per cent in the resistance of the thermometer coils, but also the resistances of the various parts of the bridge circuit other than the thermometers must not change as much as 0.003 per cent. Provision is made for testing the component parts of the bridge by the substitution of duplicate parts, which are mounted with the ratio coils of the bridge in a check box, and tests of this character are made at frequent intervals. After the apparatus had been in use for a short time a very slight change in one of the ratio coils was detected and corrected. Since that time the bridge has remained remarkably constant. It is possible also to test with the check box and recorder whether the thermometer coils remain alike in resistance at the same temperature. Provision is made in the check box for correcting slight inequalities in them by a variable shunt across a coil of small resistance in series with one of the thermometers.

## PREVENTING TRANSFERENCE OF HEAT THROUGH THE WALLS OF THE CHAMBER

In order that the quantity of heat produced in the chamber may be accurately measured, either there must be no increase or decrease in it due to the passage of heat through the walls of the chamber, or if heat is thus added or subtracted, the quantity must be determined and allowance made for it. This calorimeter is constructed and operated in accordance with the method employed in the original calorimeter of

Atwater and Rosa, to prevent gain or loss of heat through the walls, though with modifications in details which make the present apparatus exceedingly sensitive, while easy to operate. The copper wall[1] of the chamber is duplicated by a wall of zinc attached to the outside of the iron framework which supports the copper wall, as explained on page 303, and the temperature of the zinc wall is regulated to accord with that of the copper wall in such manner that the thermal conditions of the two walls will be in equilibrium with each other. When the temperature of the zinc wall is the same as that of the copper wall, the quantity of heat transmitted from each wall to the other is the same, so that neither wall actually gains heat from the other. The effect of such a condition on the quantity of heat in the chamber would be the same as if no heat were to pass from either wall to the other in either direction. If the temperature of the zinc wall is above that of the copper wall, the quantity of heat passing from the zinc to the copper is greater than that in the reverse direction—i. e., the copper wall will gain heat from the zinc wall, some of which, at least, it will transmit to the air of the chamber. Conversely, if the temperature of the zinc wall is below that of the copper wall, the former will gain heat from the latter, some or all of which the copper wall has derived from the air of the chamber. If the quantity of heat which the copper wall has gained from the zinc wall is counterbalanced by an equal quantity gained by the zinc wall from the copper wall, the effect on the measurement of the quantity of heat produced in the chamber is the same as if no heat had been transferred from either wall to the other. This counterbalancing may be accomplished by keeping the temperature of the zinc wall above or below that of the copper wall, as need be, to the same degree and for the same length of time that the conditions were reversed. For this purpose means are provided for determining when the zinc wall is warmer or colder than the copper wall, and for heating and cooling the zinc wall as is found necessary.

### Detecting Differences in Temperature of the Double Metal Walls

Thermoelectric thermometers are used to detect any difference between the temperature of the zinc wall and that of the copper wall. Differential thermoelements are installed between the two walls, with the junctions at one end of each element close to the outer surface of the copper wall, while those of the other end are in the plane of the zinc wall, and the terminals of the elements are connected with a sensitive galvanometer. The direction of the deflection of the galvanometer indicates whether the zinc wall is warmer or cooler than the copper wall—i. e., whether to warm or to cool the zinc wall.

Each thermoelement consists of four copper-constantan couples made of bare hard-drawn wire about 1 mm. in diameter (No. 18, American gauge). In making the junctions, the copper and constantan wires were put end

[1] As used in this section, the term "wall" may include the ceiling and the floor as well as the side walls.

to end and joined with silver solder. The wires were then bent at the junctions into a grid, with the parallel lines about 5 mm. apart and with copper and constantan alternating. Each constantan wire and three of the five copper wires are about 7 cm. long, so that the distance between the two opposing sets of junctions is the same as that between the copper wall and the zinc wall. The two other copper wires, which are at opposite ends of the series, are longer, to form leads for the element, as explained below.

Wire of the size stated was used chiefly because it was most readily available and seemed quite well adapted to the type of element constructed. Theoretically, a small wire would be preferable, because of smaller thermal conductance, but the support in which each element is mounted probably greatly delays change in temperature of the wires between the junctions, while affording opportunity for rapid change at the junctions. This support consists of a hard maple rod or spindle about 10 cm. in length and 15 mm. in diameter. A recess 8 mm. wide and 2 mm. deep is cut around the spindle 3 cm. from one end, and in the surface are 10 equally spaced longitudinal slots, each nearly 1 mm. wide and 2 mm. deep. The five copper and four constantan wires which, joined alternately in series in a grid, as described above, comprise the four differential thermocouples of an element, were forced into these slots until they were about a millimeter below the surface of the wood and to that extent were protected against contact with the metal sleeve and thimble by which the thermoelement is supported in the walls, as explained below. By means of a cut between two adjoining slots near the center of the spindle the copper wire at one end of the series is doubled back and extends parallel with the copper wire at the other end of the series, the two projecting from one end of the spindle and providing terminals for the element. The spindles with the wires thus embedded were boiled in paraffin for two or three hours, so that they would not swell or shrink with changes in the humidity of the air.

The temperature of the wires thus embedded in the spindle is probably that of the spindle and therefore changes slowly—i. e., the temperature gradient in each wire is quite like that of the others in the element and is relatively constant for considerable periods. On the other hand, the junctions between the copper and the constantan wires are not embedded, one series of four alternate junctions projecting into the air at one end of the spindle, while the series of opposing junctions projects into the air in the recess near the other end of the spindle, so that changes in the temperature of the air surrounding them affect the junctions quickly.

To keep each element in place between the two metal walls a short copper sleeve is passed through a hole in the zinc wall, the sleeve being soldered to the zinc at the edge of the hole to insure good thermal conductance; and directly opposite, with its open end facing that of the sleeve, a short copper thimble is firmly soldered to the outer surface of

the copper wall. A spindle is pushed through the sleeve and into the thimble until the junctions projecting from its inner end are very close to the bottom of the thimble, actual contact being prevented by the adjustment of a small screw in the end of the spindle. A change in the temperature of the copper wall immediately affects the temperature of the thimble attached to it, and consequently that of the junctions within the thimble. The junctions in the recess at the other end of the spindle are within the sleeve attached to the zinc wall, and any change in the temperature of the zinc wall affects the sleeve and, hence, the temperature of the junctions within it. Since both the sleeve and the thimble are short, neither affects the temperature of the wire in the elements any considerable distance from the junctions. The sleeve, however, projects slightly either side of the zinc wall, so that it will surround the junctions, even when they might come inside or outside the plane of the zinc, because of inequalities of distance between the two metal walls.

A short section of the spindle, between the recess and one end, projects from the outer end of the sleeve in the zinc wall and provides a firm stay for the terminals of the elements.

There are 95 such thermoelements distributed in the walls of the chamber. If they were equally spaced there would be one for each 4.5 dm. square of surface; but since the temperature of the chamber would tend to vary more at the top than at the bottom, more elements were installed in the upper than in the lower parts of the chamber to increase the sensitivity and integrate a larger number of sections of the walls. There are accordingly 16 elements in the ceiling and 10 in the floor. In the sides are five rows, with 14 elements in each row except the first one from the top, from which one is missing because the space in which it would be located is occupied by the window. The five rows are not quite equally separated, the two upper rows being slightly nearer together than the three lower ones, in accordance with the idea that the temperature of the upper section would tend to vary more than that of the lower one. These thermoelements are joined in groups in such manner that a difference between the temperature of the copper wall and that of the zinc wall may be detected in certain portions of the walls without regard to conditions in other parts. One group includes the 16 elements in the top; another the 28 elements in the two upper rows of the sides, called the upper zone; a third, the 42 elements in the three lower rows of the sides, called the lower zone; and a fourth group, the 10 elements in the bottom. The thermoelements in each group are connected in series by heavily insulated No. 18 copper wire, and the same sort of wire leads from the terminals of each group to a multiple point switch on the observer's table by which the groups may be connected successively with the galvanometer. It is also possible to connect all 95 thermoelements in series as a whole with the galvanometer and thus observe the average difference between the temperature of the copper wall as a whole and that of the zinc wall as a whole.

In the multiple-point switch the leads from the different groups of thermoelements terminate in a double row of studs arranged in segments of concentric circles, and the galvanometer leads terminate in two metal rings concentric with the studs (Pl. XXXIII, fig. 1). Metal strips, passing through a vertical shaft at the center of the circles, complete the circuit from studs to rings, the ends of the strips being bent to touch edgewise. On turning the shaft by means of the handle at the top, the strips are shifted from one pair of studs to another, thus connecting the different systems with the galvanometer. The switch includes studs not only for the thermoelement groups described above, but also for resistance thermometers described beyond, so that the same galvanometer will serve for several systems.

The galvanometer with which the electromotive forces in the thermoelement circuits are detected is a reflecting instrument of the D'Arsonval type, with a coil resistance of 39 ohms. When critically damped, it has a period of 7 seconds, and a sensitivity such that an electromotive force of approximately 2 microvolts in either circuit will cause a deflection of 1 mm. on a scale 1 meter from the mirror of the galvanometer.

With this galvanometer the number of thermoelements in each circuit is sufficient to cause a fairly large deflection when the temperature of the zinc wall is only slightly different from that of the copper wall. In the bottom section, for example, there are 10 thermoelements, the smallest number in any section, each with four differential couples, and each couple having a thermal electromotive force of close to 40 microvolts per degree of temperature difference between the junction at one end and that at the other. All 40 couples being in series, there would be a total electromotive force of 1,600 microvolts for an average difference of 1 degree between the temperature of the copper wall and that of the zinc wall in this section, or 16 microvolts for an average difference of 0.01 degree. Since an electromotive force of about 2 microvolts will cause a deflection of 1 mm., a difference of 0.01 degree would cause a deflection of at least 7 mm. It is easy to read a deflection of less than 1 mm.; consequently the effect of a temperature difference as small as 0.001 degree between the junctions at opposite ends of the thermoelements in this may be observed. The effect of such a difference in the other sections would be greater, because of the larger number of elements; the 16 in the top would cause a deflection of more than a millimeter; the 27 in the upper zone of the sides about 2 mm.; and the 42 in the lower zone more than 3 mm.

### Controlling the Temperature of the Zinc Wall of the Chamber

The temperature of the zinc wall is raised or lowered by heating or cooling the air confined in the narrow space adjacent to the outer surface of the zinc, which has a corresponding effect on the wall. Parallel with the wall, and about 4 cm. outside of it, is a wall of cork board 38 mm. thick,

which is such a good heat insulator that appreciable changes in the temperature of the air in the laboratory affect the temperature of the air confined in the spaces between the cork board and the zinc wall very slowly. The temperature of the air in this space adjacent to the zinc wall is raised by converting electrical energy into heat in a resistance wire that is strung on porcelain insulators attached to the wall; and it is lowered by passing cold water through small-bore brass pipes supported by small iron hooks screwed to the framework to which the wall is attached. Short sections of both pipes and wires and the method of attaching them to the wall are shown in Plate XXXIV, figure 2.

By wooden strips extending from the metal wall to the cork board, the air space surrounding the zinc wall is divided into sections corresponding with the top, the upper and lower zones of the sides, and the bottom of the chamber, as already described in the case of the thermo-elements in the walls. A portion of one strip is shown in Plate XXXIV, figure 2. Each section has its own heating device and cooling device, so that the temperature of the corresponding portion of the zinc wall may be controlled independently of the conditions in any other space, and the possibility of heat entering the chamber in one part of the wall and leaving it in another is prevented.

The current of water for cooling the zinc wall flows through brass pipe of about 7 mm. bore (so-called ¼-inch pipe). In the top and bottom sections the pipe extends forward and back from end to end for the whole width of the space, the successive lengths of pipe being about 15 to 20 cm. apart. In the upper and lower zones the pipe extends continuously around the four sides of the walls, the succeeding turns of the coil being about as far apart as those in the other sections. This furnishes ample cooling effect, which can be regulated by varying the temperature of the water flowing in the pipe, or the rate of flow, or both. The inlet ends of the four pipes are connected with the feed-water pipe, with the small brass needle valves used for regulating the flow in the cooling coils close together and convenient to the operator at the observer's table (Pl. XXXVI, fig. 2). The outlet ends of the coils are also brought together in a funnel below the regulating valves, so that the effect of the valves on the rate of flow may easily be seen.

The electric current for heating the zinc wall is conducted by a non-corrosive wire of a high carrying capacity, the resistance of which is about 3.5 ohms per meter. In each space the wire is distributed, as the cooling coils are, over practically the whole surface of the zinc, the successive lengths of wire extending from one end of the space to the other, about 15 cm. apart. The amount of wire in each space is such that without regulation of the current in it the heating effect would be greater than necessary. With the proper ballast resistance in series with each heater the heating effect in each section may, if desired, be made proportional to the area of zinc to be heated. In the upper zone

of the sides, for example, there is an area of about 5.8 square meters. The total resistance of the wire in the space is 143 ohms. In series with this wire but exterior to the space is a resistance unit that may be varied according to the need for current. If a unit of 200 ohms' resistance were used, there would be a little over 0.64 ampere of current flowing in the heating wire, the pressure of the current being 220 volts; and the total amount of electrical energy ($I^2R$) dissipated in the 143 ohms of wire would be nearly 59 watts, or roughly 10 watts per square meter of surface of zinc. Similarly, the area of the lower zone is about 8.9 square meters, and the resistance of the wire in it is 195 ohms; with an exterior unit of about 125 ohms in series with the heating wire, the amount of energy dissipated in the latter would be about 92 watts, or slightly over 10 watts per square meter. There are close to 2.9 square meters in the top section and the same area in the bottom, and in each of these sections is a heating coil of 117 ohms; with an exterior unit of 325 ohms in series with it, the current in each heater would approximate 0.5 ampere, and about 29 watts would be dissipated in the 117 ohms of resistance wire, or 10 watts per square meter.

In controlling the temperature of the zinc wall cold water is kept flowing continuously through the brass pipe in the air space outside of it at such a rate of flow, depending upon the temperature of the water, that the temperature of the unheated air would be lower than that at which the wall is to be kept. With a constant flow of water the temperature gradient along the pipe is quite flat in comparison with what it would be if the rate of flow were increased or decreased as the air would need to be cooled or heated; in other words, the cooling effect is fairly uniform throughout the length of the pipe. At the same time electric energy is converted into heat in the resistance wire until the air is warmed enough to bring the wall to the desired temperature. Since this dissipation of heat is equal in all parts of the wire, the total mass of air in the space is quite uniformly heated. Under these conditions to change the temperature of the wall requires only an increase or decrease of the current in the resistance wire, according to whether the wall is to be heated or cooled, which involves merely the adjustment of a rheostat in series with the wire, so that regulation is easily and quickly effected. A rheostat of oxidized constantan wire wound on an enameled metal tube and having a sliding contact passing over successive turns of the wire, with a resistance of about 980 ohms and a current-carrying capacity of 1 ampere, is in series with the resistance wire comprising the heating coil in each section. The four rheostats for the different air sections to be controlled are attached vertically to an asbestos slab at one end of the observer's table, as seen in Plate XXXVI, figure 1, with the sliding contacts in easy reach of the operator reading the galvanometer deflections.

The temperature of the zinc wall is kept as nearly as possible like that of the copper wall, so that the deflections of the galvanometer connected with the differential thermoelements in the walls are as close as possible to 0. Even under the most favorable conditions it is hardly practicable to keep the two walls so uniformly alike that there will be no deflection at any time, because the temperature of the copper wall, however well regulated, does vary to some extent, and it is not possible to anticipate the change. It is possible, however, to keep the deflections most of the time so small that any error introduced by the temperature differences which they indicate would be insignificant. As explained on page 334, the number of thermoelements in each section of the walls and the sensitivity of the galvanometer are such that a very small difference between the temperature of the copper wall and that of the zinc wall would cause a fairly large deflection; hence, a very small deflection really means a practical identity of temperature of the two walls. When the rate of production of heat within the chamber is quite uniform and the rate of abstraction of heat is so nearly like it that the temperature conditions within the chamber are quite constant, the temperature of the zinc wall may be kept so nearly like that of the copper wall that the deflection will not exceed 5 mm. and will generally be less. A deflection of that magnitude would indicate for the bottom section a difference not greater than 0.005 degree between the average temperature of the copper floor of the chamber and that of the zinc wall outside of it; for the other sections it would indicate still smaller differences. The amount of heat gained by either wall from the other with such small differences is of little importance in comparison with the total amounts usually measured in the chamber. In an experiment with a variable heat production, as would be the case with a man moving and quiet by turns, such a close balance could hardly be maintained at all times, though the deviation need not greatly exceed 5 mm. for any considerable periods. Furthermore, it is possible to make the deflections in one direction equal to those in the other direction for equal short periods, so that whatever heat may be gained by the copper wall from the zinc wall during one period is counterbalanced by that gained by the zinc wall from the copper wall during the succeeding period, in which case there is no actual increase or decrease of the quantity of heat in the chamber for the total time of the two periods due to an exchange of heat between the walls.

In order that the walls controlled in the manner described shall be heatproof, their temperature and that of the iron structure between them must be the same. The temperature of the copper wall, and consequently that of the zinc wall, is governed by that of the air in the chamber; but the two walls may be brought into thermal equilibrium at a temperature above or below that of the framework, in which case the quantity of heat in the chamber would probably be affected by the

mass of iron with its large thermal capacity and high conductivity, the magnitude of the effect depending upon the difference between the temperature of the iron and that of the air in the chamber. To avoid error from this source in the measurement of the heat generated in the chamber it is very essential not only to keep the temperature of the walls of the chamber and that of the air of the chamber as nearly alike and as constant as possible during the period in which the measurements are made, but also to be certain that at the beginning of the period the temperature of the iron structure is identical with that at which the walls and air are to be kept. To this end the regular experimental period must be preceded by a period in which the walls and their supporting structure are brought to the desired temperature. The length of this period depends upon the temperature conditions of the walls when it begins, but it is shortest when the temperature of the walls and framework is kept under control by means of a thermoregulator in the chamber during the periods in which experiments are not in progress. With care and attention to the details outlined it is possible to prevent gain or loss of heat through the walls of the chamber, but the amount of attention and manipulation necessary to avoid error because of the metal would be avoided if the framework were constructed of material having small thermal capacity and poor conductivity. Such a change would be made in reconstructing the calorimeter.

### PREVENTING GAIN OR LOSS OF HEAT IN THE AIR ENTERING AND LEAVING THE CHAMBER

Provision is also made against loss or gain of heat in the circulating air. A thermoelement of 40 couples is installed with one end of each couple in the incoming air just as it enters the chamber and the other end in the outgoing air just as it leaves the terminals of the element leading to the multiple point switch on the observer's table, by which it may be connected with the galvanometer. Any difference between the temperature of the ingoing air and that of the outgoing air indicated by the galvanometer is corrected by heating or cooling the ingoing air as needed. A copper tube of small bore is coiled tightly on the brass pipe that conducts the air into the chamber for a distance of about 30 cm. just before the pipe enters the wall, and through this coil water runs continuously, tending to keep the air too cool. Adjacent to this, also on the brass pipe, is an electric heating coil of about 800 ohms' resistance, which warms the air to the desired temperature. To change the temperature of the air, only the current in the heating coil is varied. In series with this coil is a tube rheostat of about 2,500 ohms' resistance by which the current in the resistance coil and, hence, its heating effect are regulated, the position of the sliding contact being adjusted until the galvanometer indicates that the temperature of the ingoing air is the

same as that of the air leaving the chamber. This rheostat is mounted on the end of the observer's table beside those for controlling the temperature of the zinc wall.

### ALLOWANCE FOR CONDITIONS AFFECTING THE HEAT OF THE CHAMBER

Any passage of heat into or out of the chamber through the walls or in the ventilating air current being prevented, the sum of the quantity of latent heat in the water vapor of the outgoing air and that of sensible heat removed by the water circulating in the heat absorber would equal that actually produced in the chamber if there were no change in the temperature of the walls or in that of any objects confined within them. Under ordinary conditions, however carefully the rate of abstraction of heat from the chamber has been regulated to accord with that of production, temperature changes can not be absolutely avoided, so they must be measured and allowance made for them.

#### CHANGE IN TEMPERATURE OF THE METAL WALLS

If the temperature of the copper wall is lower at the end of a given period than it was at the beginning, and the temperature of the zinc wall has been kept identical with that of the copper wall throughout the period, a certain amount of heat has been imparted to the air of the chamber by the copper wall during the period; or, conversely, if the copper wall is warmer at the end of the period, some heat has been absorbed from the air by the wall. To ascertain how much allowance must be made for the heat involved in such changes, it is necessary to determine the temperature of the copper wall at the beginning and the end of the period and to know how much heat is necessary to raise the temperature of the calorimeter a given amount—i. e., its hydrothermal equivalent.

The temperature of the copper wall is determined by means of an electric-resistance thermometer somewhat like that described on page 313 for determining the temperature of the air. In this thermometer, however, each of the six coils of nickel resistance wire is wound on a thin fiber strip about 12 cm. long and 1 cm. wide, and is covered with a thin layer of silk and lacquered, the completed bulb being about 1.5 mm. thick. A strip of brass, slid into guides soldered to the copper wall, presses each coil firmly against the wall so that there is close thermal contact with metal on each side of the coil; hence, changes in the temperature of the wall affect the resistance wire very quickly. These six coils, joined in series by well-insulated No. 16 copper wire, are distributed on the side walls and ceiling in such manner as to show the average temperature of the total mass of copper. The terminals of the series of coils are connected with the special switch, mentioned on page 334, and through that with the temperature indicator (Wheatstone bridge) on the observer's table. The bridge and galvanometer are sensitive to resistance changes

in the thermometer coils that would result from a change of 0.01 degree in the temperature of the copper wall.

The hydrothermal equivalent of the calorimeter has been estimated from determinations of the quantity of heat that had to be dissipated in the chamber to raise the temperature of the copper wall 1 degree, and the amount of heat that was imparted to the air of the chamber when the temperature of the copper wall fell 1 degree, while the thermal conditions of the zinc walls were kept in equilibrium with those of the copper wall during the change. The capacity for heat as determined in both ways was not far from 40 Calories. From the weights and specific heats of the materials entering into the construction of the chamber the hydrothermal equivalent was calculated to be between 35 and 40 Calories. According to these figures, the quantity of heat in the chamber should be increased by 40 Calories with a fall of 1 degree, or decreased by 40 Calories with a rise of 1 degree in the temperature of the copper wall, if the thermal conditions of the zinc wall were in equilibrium with those of the copper wall while the change occurred.

This will be the case, provided the change in thermal conditions has occurred in such manner as to affect the iron supporting structure the same as the copper wall. In constructing the calorimeter no provision was made for determining the actual temperature of the structure, the assumption being that the thermal conditions of the iron framework would also be controlled by the regulation of those of the zinc wall, so that the temperature of the iron would be quickly brought to that of the copper wall and would vary with it. Experience has shown, however, that in some circumstances the change in thermal conditions of the iron may lag somewhat behind that of the copper wall; hence, it is much more desirable to keep the temperature of the walls of the chamber as constant as possible for the whole length of an experimental period than to depend upon the correction for change in temperature. With a sudden change in the rate of dissipation or absorption of heat in the chamber near the close of a period, which would affect the temperature of the copper wall, there might be an error in the measurement of heat for the period in spite of the allowance for temperature change. (See p. 346.)

### Change in Body Temperature of the Subject of an Experiment

When the human body is the source of heat in the chamber, allowance must be made for the heat involved in any change in its temperature, as the body has a considerable thermal capacity. From the best available data it would appear that a change of 1 degree in the temperature of the body involves a change of 0.83 Calorie in the quantity of the heat accumulated for each kilogram of body weight. A rise in body temperature would mean that the store of heat in the body has been increased a certain amount, which would have to be added to that eliminated by the body and measured by the calorimeter during the period in which the rise

occurred in computing the quantity of heat actually produced by the body in the period. Conversely, a decrease in body temperature would mean that a certain amount of the heat that had accumulated in the body previous to the experimental period had been eliminated with that produced by the body during the period and should be subtracted from the quantity measured by the calorimeter in determining the quantity actually produced in the period.

The weight of the body can be ascertained accurately. The specific heat assumed is an estimate, but is probably fairly accurate. The temperature of the body as a whole can not be determined precisely, because it is not the same in all parts of the body. The temperature at the surface is noticeably lower than that of the interior, and that of the tissue in one region differs from that of the tissue in another. It seems probable, however, that, except perhaps at the surface, a change in temperature in one part of the body is accompanied by a corresponding change in the others; hence, the amount of temperature change, which is the factor concerned in the correction here considered, may be ascertained with a fair degree of accuracy from measurement of temperature where possible, but preferably below the surface.

By means of an electric-resistance thermometer the temperature of the subject in the chamber, at the spot at which the thermometer is located, may be ascertained at any given moment by the observer outside. A coil of wire of variable resistance, mounted so that it may be worn by the subject and kept at the temperature of the body, is connected with a Wheatstone bridge on the observer's table, by which the variations in resistance of the coil, due to changes in body temperature, may be observed, connection between the bridge and the thermometer coil being made through the special switch mentioned on page 334.

One type of thermometer bulb, designed for use in the rectum, is a coil of platinum wire having a resistance of 20 ohms at 37° C., inclosed in a thin steel shell or capsule 5 cm. in length and 5 mm. in external diameter. Since this thermometer may be kept in place for considerable periods without discomfort, a virtually continuous record of body temperature may be obtained, depending upon the frequency of the readings by the observer, and fluctuations may be followed for long or short periods as desired, but the temperatures at the beginning and end of the experimental period are the ones essential for the correction here considered. In another type, designed for measuring temperature of the body surface, the wire is wound in a flat spiral coil 15 mm. in diameter, mounted in a frame of thin, hard rubber by which it may be held against the skin. This coil rapidly acquires the temperature of the skin.

In some cases the temperature is measured by means of accurate clinical thermometers, inserted by the subject under the tongue or in the axilla, which are afterward read by the observer.

HEAT FROM OTHER SOURCES

The store of heat in other objects in the chamber than the body of the subject—e. g., furniture—is increased by a rise and decreased by a fall in the temperature of the air surrounding them, and allowance must be made for the effect of such change in their condition upon the measurement of the quantity of heat produced in the chamber. The quantity of heat involved is computed from the weight, the specific heat, and the change in the temperature of the objects. The latter factor is not definitely known, however, as no provision is made for actually measuring the temperature of such objects; the assumption being that their change in temperature will be the same as that of the air, which is determined. Where the change occurs slowly, any error involved in such assumption is probably negligible; but this is not true when any considerable change occurs in a short period. This is another reason for keeping the temperature of the air of the chamber as constant as possible.

Allowance must be made also for gain or loss of heat due to the introduction of objects into the chamber at a temperature above or below that of the air. Hot food or drink, for example, admitted through the food aperture would add heat to that produced in the chamber, while cold material would absorb some of the heat produced. The temperature at which any material is admitted is recorded, together with its weight and character, and from these data, with the specific heats of the various articles, the necessary corrections are computed.

The electric fan by which the air of the chamber is agitated and the electric light, when one is used, both generate heat which forms part of that measured by the calorimeter and for which allowance must be made. The quantity of heat produced is computed according to the formula $\frac{EIt}{4.183}$ = small calories at 20° C., $E$ being the voltage and $I$ the amperage of the current in the lamp and the fan, and $t$ the time in seconds during which it was used.

The divisor, 4.183, is the number of international joules (watt seconds) equivalent to one small calorie at 20° C. (10, p. 255). The lamp and fan are connected in such manner that the voltage and amperage of both may be determined at the same time by calibrated measuring instruments on the observer's table, the readings of which are recorded at regular intervals. That the heat may be generated at a uniform rate, the current is taken from a generator which has an automatic regulator to keep the voltage constant within quite narrow limits.

## APPARATUS FOR MEASURING MUSCULAR WORK PERFORMED BY THE SUBJECT OF AN EXPERIMENT

For the study of many problems involving the performance of muscular work some method of measuring the amount of work done is requisite. An apparatus (9, p. 48; 8, p. 11) that was devised in connection with the nutrition investigations of the Department has proved very

successful for measuring work done with the muscles of the legs. The principle of the device is that of the electric brake. It is designated a "bicycle ergometer," since it bears some resemblance to a bicycle; in fact, in its construction all of a bicycle except the wheels was used, and the work done in operating it is of the same kind as that involved in propelling a bicycle. In the ergometer, however, the front wheel of the bicycle is replaced by a pedestal and the rear part of the frame is supported by a rack, so that a heavy copper disk, 40.5 cm. in diameter and approximately 6 mm. in thickness, which replaces the rear wheel of the bicycle, will rotate freely on its ball-bearing axis. An electromagnet is attached to the frame, with its poles on opposite sides of the disk, with the inner edge of the rectangular-pole faces coincident with the circumference of the disk, and with the face of each pole 1 mm. from the surface of the side of the disk. When there is no current in the field coils of the magnet, the amount of energy required to cause the disk to rotate between the pole faces is small, being merely that necessary to overcome the friction of the bearings and the resistance of the air against the moving parts; but when there is a current in the coils, with its resulting magnetization, currents are induced in the disk rotating in the magnetic field, which tend to prevent it from rotating. The brake effect depends upon the flux density of the field, which varies with the strength of the magnetizing current. The amount of work done by the subject on the ergometer is therefore easily controlled by adjusting a rheostat in series with the coils of the magnet until the strength of the current is that which will result in the desired resistance to be overcome in causing the disk to rotate. A particular advantage in this apparatus is the constancy and uniformity with which the effect may be reproduced.

The power applied to the pedals when work is done on this ergometer is converted into heat, a small part of it by the friction of the moving posts of the mechanism and the rest by the energy transformations in the disk. The quantity of heat thus produced varies with the intensity of the magnetic field and also with the rate of rotation of the disk. From calibration of the ergometer in the calorimeter the amount of heat produced by each rotation of the disk in the magnetic field was determined for a considerable variety of conditions of velocity of the disk and strength of magnetizing current within the range commonly employed in experiments. By use of curves derived from the data of calibration the heat equivalent of the external muscular work performed by the subject on the bicycle ergometer is computed directly from the total number of rotations of the disk, as shown by an automatic counter, and of strength of current in the field coils, as shown by an accurate ammeter.

The heat produced in the ergometer is measured by means of the calorimeter, together with that eliminated from the body; but since the former can be ascertained, as just explained, it may be subtracted from the total heat measurement, when the amount of heat produced by the subject in performing muscular work is computed.

## TESTS OF THE ACCURACY OF THE RESPIRATION CALORIMETER

At frequent intervals the accuracy with which the respiration calorimeter will function is tested by burning ethyl alcohol in the chamber in such manner as to insure complete combustion and measuring with the apparatus the amounts of oxygen consumed and of carbon dioxid, water vapor, and heat produced. Commercial alcohol, pure in quality and containing about 90 per cent of ethyl hydroxid, is satisfactory for the purpose. The actual percentage is ascertained from determination of the specific gravity of the alcohol. The amount of oxygen that would be required to burn 1 gm. of the commercial alcohol, and the amounts of water vapor and carbon dioxid that would result from the combustion, are computed from the chemical equation for the reactions occurring in the combustion of ethyl hydroxid, with allowance for the water present in the sample burned. The heat of combustion of ethyl hydroxid at constant pressure is taken as 7.08 Calories per gram.

The burner used in these experiments was made of two concentric tubes of thin brass 5 cm. in length, the outer tube being 18 mm. in external diameter. At the lower end each tube is soldered to a brass ring, which provides an annular space between them 3 mm. wide, in which is a wick of asbestos; and as the inner tube is open at both ends, there is a center draft for the flame. No products of incomplete combustion have been found in the air of the chamber during a test in which alcohol was burned with this burner.

The burner is soldered to one end of a piece of 4-mm. copper tubing, the other end of which passes through the wall of the chamber to the alcohol supply outside, from which the burner is fed in such manner that the rate of consumption is uniform. Attached to the outer end of the copper tube is an elbow of 4-mm. glass tubing, with a side outlet in the vertical arm to provide for an overflow. The height at which this outlet is set with relation to the top of the burner governs the rate of consumption of the alcohol. The level having been fixed, alcohol is fed into the vertical tube so that some of it will drop regularly from the outlet. The rate of combustion in the chamber is then very constant. The overflow alcohol is caught in a small bottle, which is weighed with the supply flask at the end of each period, the loss in weight of both containers showing the quantity of alcohol burned. The connection between the overflow bottle and the outlet and also that between the supply flask and the feed tube are such that the loss of alcohol by evaporation is negligible.

The results of alcohol check tests of the respiration calorimeter indicate that the determinations made with it are at least sufficiently accurate for investigations of the character in which it is used. This is shown by the data in Table II, which summarizes the results of two tests selected from many equally good.

In November, 1913, in a 3-hour period, 56.3 gm. of commercial alcohol containing 88.32 per cent of ethyl hydroxid were burned to test the

accuracy of the determinations when heat was produced in the chamber at a rate of about 120 calories per hour. For all four factors the quantities determined were slightly larger than those computed from the composition of the alcohol, the discrepancies amounting to 1.5 per cent for oxygen, 0.7 per cent for water, and the same for heat, and 0.2 per cent for carbon dioxid. The respiratory quotient—i. e., the ratio of the volume of carbon dioxid produced to that of oxygen consumed in the combustion of alcohol—is 0.667; in the test the ratio of the values found was 0.658. Similarly, the ratio of the number of Calories of heat produced to the number of grams of carbon dioxid produced is theoretically 3.705, whereas in the test it was 3.725.

TABLE II.—*Data obtained in the combustion of alcohol in the respiration calorimeter*

| Date. | Oxygen. | | Water. | | Carbon dioxid. | | Heat. | | Quotients. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Found. | Required. | Found. | Required. | Found. | Required. | Found. | Required. | Respiratory ($CO_2$: $O_2$). | Thermal (Cal.: $CO_2$). |
| | *Gm.* | *Gm.* | *Gm.* | *Gm.* | *Gm.* | *Gm.* | *Cal.* | *Cal.* | | |
| Nov. 21, 1913... | 105. 1 | 103. 6 | 65. 4 | 64. 9 | 95. 1 | 94. 9 | 354. 2 | 351. 7 | 0. 658 | 3. 725 |
| Feb. 18, 1915... | 139. 0 | 140. 7 | 97. 3 | 98. 5 | 142. 5 | 143. 9 | 535. 8 | 533. 3 | . 669 | 3. 759 |

In February, 1915, in a 6-hour period, 85.35 gm. of commercial alcohol containing 88.25 per cent of ethyl hydroxid were burned, the rate of production of heat being about 90 Calories per hour. In this test the heat measured by the calorimeter was nearly 0.5 per cent greater than that computed, whereas the quantities of oxygen, water, and carbon dioxid measured were 1 to 1.3 per cent lower than those computed.

Another test made at frequent intervals provides a check on the accuracy of the calorimetric function of the apparatus. Electric energy is converted into heat within the chamber, and the amount produced in a given period, which can be computed very accurately, is compared with that measured by the calorimeter during the period. The electric energy is converted into heat in a coil of resistance wire suspended in the chamber. The amount of energy that is dissipated is computed from the values for the voltage and amperage of the current in the coil, the time in seconds, and the factor for converting watt seconds to small calories at 20° C., as explained on p. 342.

The resistance of the heating coil depends upon the desired heat production, the majority of the tests having been made with a coil having a resistance of 440 ohms, which allows 0.5 ampere of current to flow with a fall of potential of 220 volts. The resultant heat is approximately 95 Calories per hour, or about that produced by an average man sitting still. That the rate of production of heat may be constant, the voltage of the current is controlled by an automatic regulator; but the actual fall in potential is measured by a voltmeter connected to the terminals

of the coil, and the amperage of the current is measured by a milliammeter in series with it, the readings of both meters being recorded every minute, or oftener.

In a 2-hour test in January, 1915, the total heat production was 139.00 Calories, while the quantity measured with the calorimeter was 139.04 Calories. Such absolute agreement is not to be expected invariably, though with the conditions ordinarily prevailing in an electric check the two values should not differ by as much as 1 per cent. A discrepancy of that size would indicate need of attention to some part of the apparatus, or lack of attention to some details of operation. For example, in a 3-hour test in February, 1915, the total quantity of heat generated in the chamber was 370.19 Calories and that measured by the calorimeter was 377.39 Calories. The discrepancy between the two values was due to a considerable decrease in the temperature of the walls of the chamber during the last half of the first hour, resulting from a lowering of the temperature of the water entering the heat absorber. In the two hours following that the heat production was 245.87 Calories, as computed, and 246.75 Calories, as measured, a discrepancy of less than 0.4 per cent. The results in the first hour illustrate the statement made on page 340 regarding error in heat measurement when the temperature of the copper wall changes so quickly that its thermal conditions differ from those of the iron structure to which the wall is attached.

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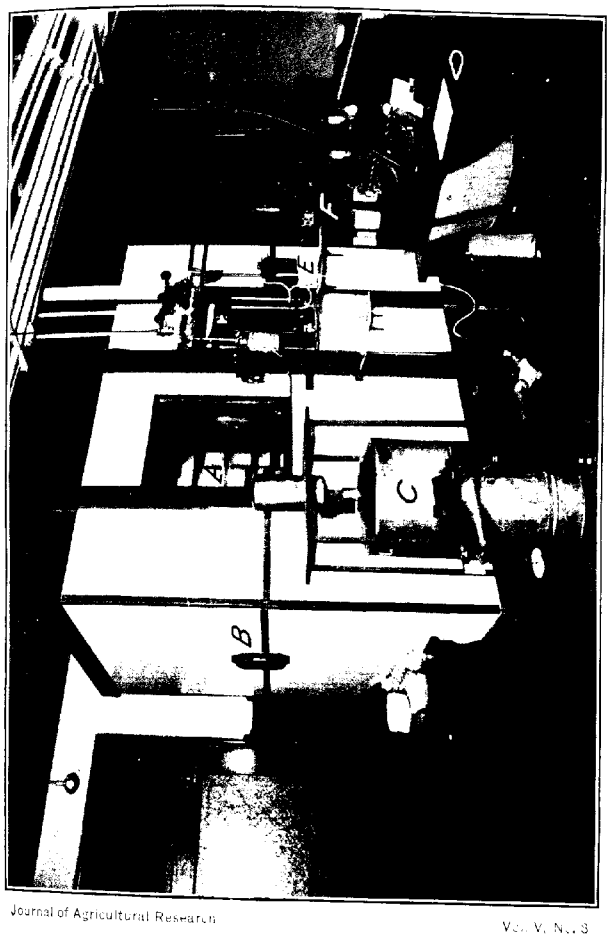
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## PLATE XXX

General view of the respiration calorimeter: *A*, Opening serving as door and window to chamber. *B*, Food aperture. *C*, Tank to catch water coming from the heat absorber in the chamber. *D*, Observer's table, with devices for measuring and regulating temperatures. Other temperature measuring and regulating apparatus pertaining to the calorimeter are not shown in this view. *E*, Thin rubber bag, resting on shelf, to serve as air tension equalizer. *F*, Table on which are motor and blower for maintaining circulation of air through chamber, and absorbers for purifying the air.

Improved Respiration Calorimeter

PLATE XXX




A
B
B
C
A
D
D


C
A
B
B

## PLATE XXXI

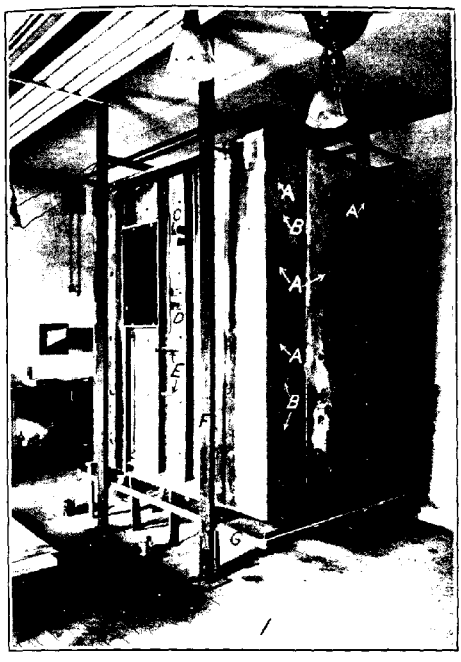
Fig. 1.—Structural iron framework for respiration chamber: *A*, Sills and ceiling plates of angle iron; *B*, studding and joists of light weight channel iron, with narrow edge; *C*, asbestos building lumber to support copper floor; *D*, supports for exterior cover of cork board and museum board.

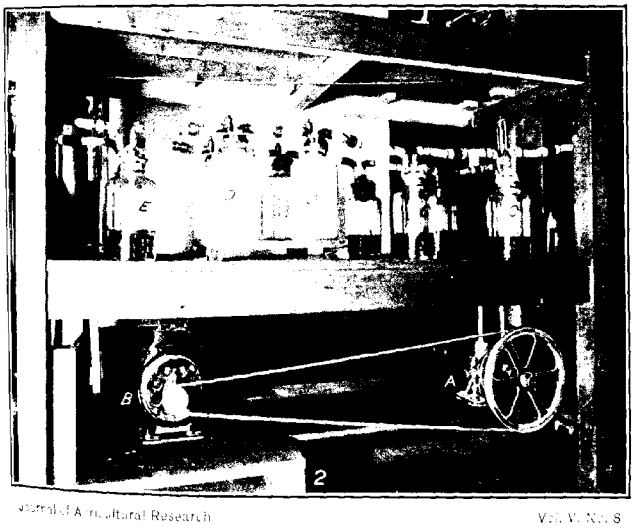
Fig. 2.—Copper-walled chamber attached to inside of iron framework: *A*, Bolts for attaching wall to structure; *B*, wooden insulation between iron and copper; *C*, thimbles soldered to outside of copper wall to receive inner end of thermoelement described on page 331.

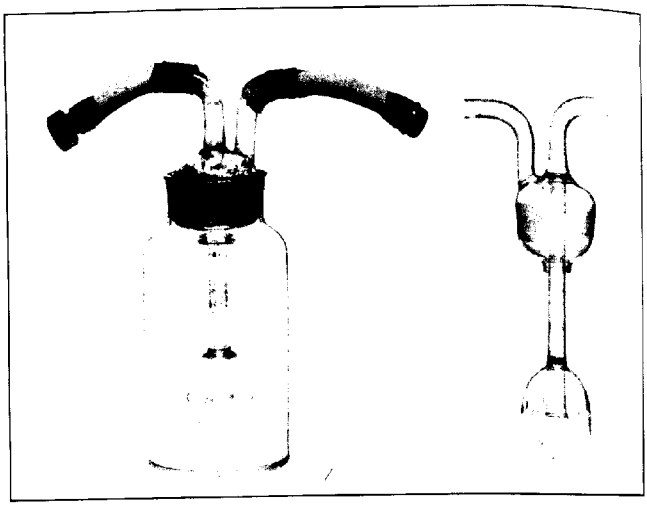
## PLATE XXXII

Fig. 1.—Zinc wall attached to outside of iron framework, with all but the last section shown in place: *A*, Openings in zinc wall to admit thermoelements as described on page 332; *B*, hooks projecting outward from edge of channel irons, to support water pipe for cooling zinc, as explained on page 335; *C*, sheet-metal tubes projecting from holes in copper wall for passage of pipes for air entering and leaving the chamber, as explained on page 304; *D*, tubes projecting from holes in copper wall for passage of pipes for water entering and leaving the heat absorber, as explained on page 316; *E*, passages for pipe carrying oxygen into the chamber (see p. 309), for wires for electric fan, electric light, resistance thermometers, etc.; *F*, supporting structure for chamber; *G*, supporting structure for cork board and outer covering.

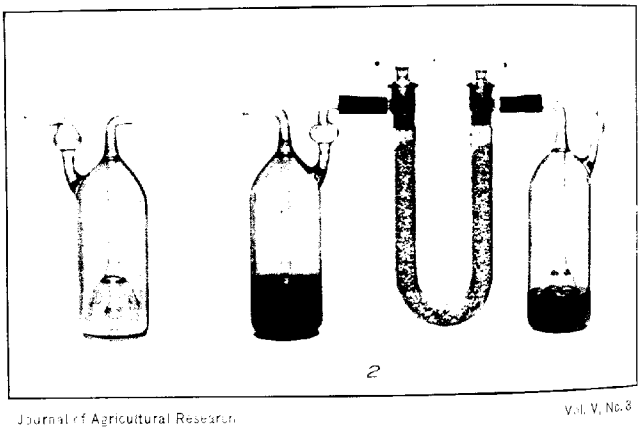
Fig. 2.—Devices for circulating and purifying air: *A*, Rotary compressor for maintaining air circulation; *B*, motor for driving compressor; *C*, special bottles containing sulphuric acid, for removing water vapor from circulating air; *D*, bottles containing soda lime for absorbing carbon dioxid from circulating air; *E*, bottle containing sulphuric acid for absorbing water vapor given up by the soda lime.


A
B
A'
A
A
B
C
D
E
F
G
1


E
B
A
2



1



2

## PLATE XXXIII

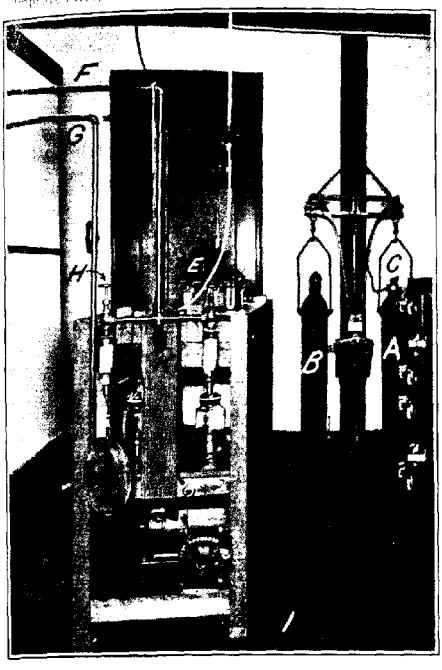
Fig. 1.—Special container for sulphuric acid to remove water vapor from air passing through it. At the right is a stopper with the entrance and exit tubes, as described on p. 306.

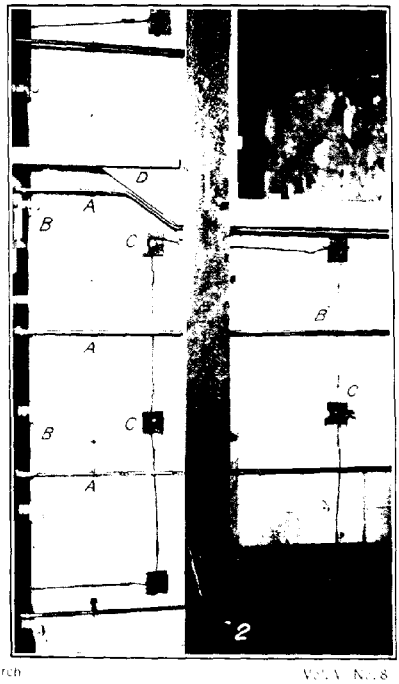
Fig. 2.—A small absorber train for removing water vapor and carbon dioxid from sample of residual air. An empty acid bottle is shown at the left.

## PLATE XXXIV

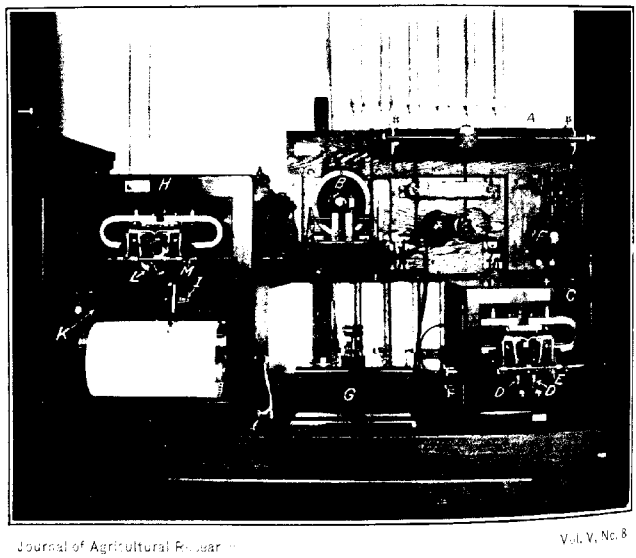
Fig. 1.—Balance for weighing oxygen cylinder and end view of absorber table: *A*, Cylinder containing oxygen under pressure; *B*, empty cylinder for counterpoise; *C*, valve for reducing pressure of oxygen from cylinder; *D*, rubber bag to collect sample of air for determination of residual oxygen; *E*, meter for measuring sample of air for determination of residual moisture and carbon dioxid; *F*, pipe for air returning to chamber; *G*, pipe for air coming from chamber; *H*, valve for closing circulating air system between absorbers and ingoing air pipe; *I*, trap for removal of sulphuric-acid spray from returning air; *K*, point at which air from meter is restored to air returning to chamber.

Fig. 2.—Method of attaching heating and cooling systems to zinc wall: *A*, Hooks of iron wire, screwed into metal framework, supporting brass pipe for cooling zinc wall; *B*, porcelain insulators, carrying resistance wire for heating zinc wall; *C*, exterior ends of wooden supports of thermoelements projecting from zinc wall; *D*, wooden strip, dividing air space adjacent to zinc side walls into upper and lower zones.


F
G
H
E
B
C
A
1


D
A
B
C
A
B
C
A
B
C
2


E
C
B


A
H
L
M
K
G
C

## PLATE XXXV

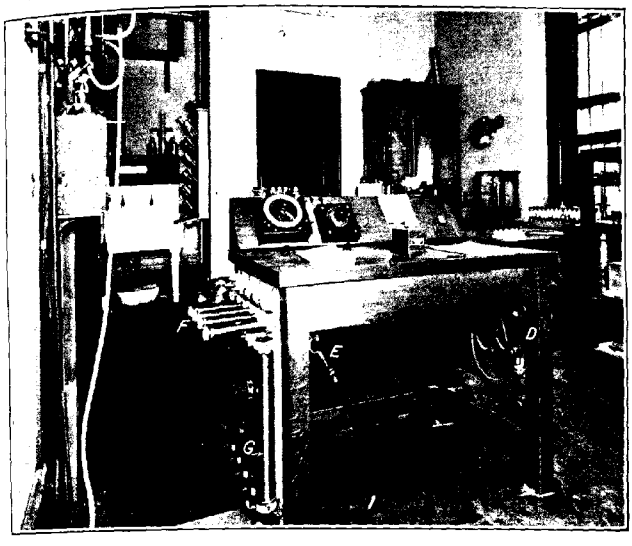
Fig. 1.—Interior of respiration chamber with subject as seen through the window: *A*, Units of the electric-resistance thermometer for determining temperature of the air; *B*, telephone for communication with observer; *C*, push button to call observer; *D*, electric fan to stir the air; *E*, portion of heat-absorbing device described on page 316; *F*, unit of electric-resistance thermometer to measure temperature of copper wall; *G*, small electric lamp for convenience of subject.

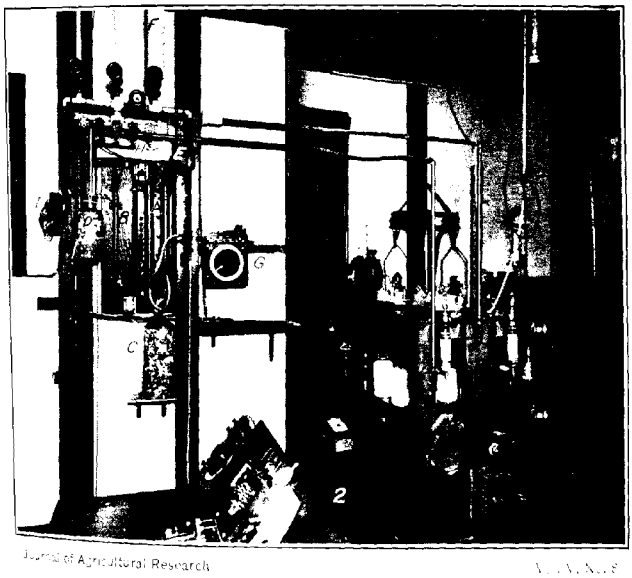
Fig. 2.—Apparatus for regulating and measuring the temperature of water for absorbing heat: *A*, Rheostat in series with heating coil in final heater; *B*, differential motor for adjusting sliding contact on rheostat; *C*, mechanism for governing activity of motor B, in accordance with deflections of galvanometer mounted in the apparatus; *D*, contact keys for shunting field windings of motor *B*; *E*, shaft turning cams which operate contact keys; *F*, motor driving cam shaft; *G*, special Wheatstone bridge for differential resistance thermometers, containing also devices for varying the range of the slide wire and for checking the precision of the apparatus; *H*, mechanism for shifting balancing contact on slide wire, according to deflections of the galvanometer mounted in the apparatus. The slider *I*, carrying the contact on the slide wire mounted in bar *K*, is moved in either direction by a cord pulled by the shaft bearing large wheel *L*, which is turned by small gears on shaft *M*, driven by a small motor behind the mechanism. A pen carried by the slider draws a temperature difference curve showing the movement of the contact on the slide wire.

## PLATE XXXVI

Fig. 1.—Observer's table: *A*, Multiple-point switch for connecting electric measuring circuits with the galvanometer; *B*, Wheatstone bridge (temperature indicator) for measuring temperatures of air in the chamber, of the copper walls, and of the body of the subject; *C*, galvanometer used with the switch and the bridge. The instrument shown here is simply a substitute for a much more sensitive galvanometer which does not appear in this view; *D*, telephone for communication between the observer outside and the subject inside the chamber; *E*, push button to call the subject; *F*, resistance units in series with heating coils outside of zinc wall, as explained on page 336; *G*, rheostats to control currents for heating zinc walls.

Fig. 2.—Devices for regulating temperature of water for heat absorber: *A*, Preheater, adjusted by hand; *B*, final heater, adjusted automatically, having an electric heating coil in the bottom and a resistance thermometer coil in the top of the tube; *C*, bottle filled with pumice, for mixing water flowing from preheater to final heater; *D*, bottle for mixing water flowing from final heater to heat absorber; *E*, special cock to regulate rate of flow of water in heater; *F*, pipe bringing chilled water from cooler to preheater; *G*, temperature indicator connected with thermometer in final heater; *H*, needle valves to regulate flow of water to cool air space adjacent to zinc wall; *I*, exterior ends of electric-resistance thermometers in water entering and leaving heat absorber. Leads from these thermometers extend to the bridge marked "G" in Plate XXXV, figure 2.


E
D
G
1


G
C
2

# OCCURRENCE OF MANGANESE IN WHEAT

By WILLIAM P. HEADDEN,
*Chemist, Colorado Agricultural Experiment Station*

The presence of manganese in various plants has been observed repeatedly. It is now stated that it has been shown to be present and has been determined in a great many grains, roots, leaves, and whole plants and that it is probably present in all plants.

It is generally asserted that this manganese is to be considered as an accidental constituent and that it has no physiological function. An opposite view, however, is held by some who maintain that it performs an important catalytic function in the plant. Bertrand, for instance (1),[1] has shown that the enzym laccase can not act as an intermediary between the oxygen of the atmosphere and certain organic compounds in the cells of the plants if it is deprived of its manganous oxid, with which it forms a feeble compound. He has further shown that this enzym, laccase, is very generally diffused throughout the vegetable kingdom and that whenever laccase functions in the nutrition and growth of plants, manganese is a necessity. The amount of manganese contained in this laccase is only 0.12 per cent.

There are some data on the effects of manganese on wheat, oats, barley, grass, etc. Guthrie and Cohen (3) attribute the death of grass on certain spots to the presence of 0.254 per cent of manganic oxid in the soil. They account for the death of barley in certain soils in the same manner. Voelcker (7), experimenting with different salts of manganese, applied in quantities up to 200 pounds per acre, obtained results which are summarized as follows for experiments with wheat:

> The chlorid and nitrate produced a good color in the plants. The iodid distinctly retarded germination and growth. The untreated plots produced as good plants as any of the others except those which had received an application of nitrate or phosphate. The phosphate, chlorid, sulphate, and red oxid ($Mn_3O_4$) each gave an increase in yield.

Kelley (6) states that some plants vegetate normally in the presence of manganese salts, others are stunted in growth and die back from the tops of the leaves, which turn yellow or brown and sometimes fall off. Plasmolysis is produced. Chlorophyll may be destroyed as in the pineapple. The ash shows an increased percentage of manganese. The percentage of lime is increased and that of the magnesia is decreased. This ratio, on the authority of Loew, is considered an important one. The absorption of phosphoric acid is lessened. The formation of manganous phosphate is suggested as the possible cause of this.

[1] Reference is made by number to "Literature cited," p. 355.

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Nov. 22, 1915
Colo.—1

According to Kelley, the action of manganese, especially if present in the soil in relatively large quantities, 2.34 to 9.74 per cent, produces very radical changes in the nutrition of the plant (5). But such quantities of manganese as correspond to these percentages are not often found in soils.

Brenchley (2, p. 583) sums up her observations on the effects of manganese on barley thus:

> Manganese sulfate, though not an actual toxic to barley, retards the growth very considerably if supplied in moderate quantities. Minute traces of the salt have a decided stimulative action both on the root and shoot. * * * When supplied in sufficient concentration manganese is taken up by the plant and deposited in the lower leaves.

Jost (4, p. 87), in treating of the nonessential ash constituents absorbed from the soil by plants, says of silica:

> Although silica may be quite superfluous from the chemical point of view, it may be of great service to the plant in the biological sense. Our knowledge of these subjects, despite the amount of work which has been expended on them, is still very imperfect, and it is possible to defend the assertion that all the ash constituents have definite functions to perform, although these have not as yet been determined in all cases, and although these constituents can not be considered as taking part in metabolic changes. * * * The occurrence of manganese may, however, be specially noted, as leading to the consideration of a new series of phenomena. It is not widely distributed in the earth, and yet is found, though only in traces, in very many plants.

In discussing nutritive and stimulative materials he uses the following language concerning iron (4, p. 88):

> This distinction is not readily made out in all cases; iron, for example, is a difficult element to deal with, because it is essential only in the minutest traces, and is possibly both a nutrient and a stimulant.

Iron is definitely recognized as essential for the growth of plants, though the quantities required are exceedingly small.

The presence of manganese in wheat straw has been mentioned by others, but nowhere have I found its quantity given, and it is not mentioned in connection with the grain. The statement of M. Bertrand (1) that "manganese has been found in many grains" [1] is the only one known to me that may indicate the occurrence of this element in the wheat kernel.

In examining the mineral constituents of wheat (*Triticum* spp.) I was struck by the fact that there was uniformly enough manganese present to come down with the calcic oxalate and to impart a decided brown color to the calcic oxid when ignited. A few preliminary determinations revealed the fact that there was as much or more manganese than iron present. At the time this observation was made I had examined 25 samples of wheat and had found manganese present in every sample. These samples had been grown on the same soil, though the different plots had not received the same fertilization. The supply of manganese

[1] Author's translation.

in the soil is about 0.10 per cent, calculated as elemental manganese. If the manganese be an accidental constituent, as is usually held to be the case, its presence must be due to the supply in our soil, but the amount taken up appears to be very nearly constant, irrespective of the soil.

In order to ascertain whether the manganese is universally present in the wheat kernel and to determine in what quantity it is usually present, I obtained samples of wheat from a number of localities in the United States and Canada and from three European countries. While manganese is probably present in every cultivated soil, it is very rarely the case that it constitutes more than a small fraction of 1 per cent, while iron is usually present in much more considerable quantities. The amount of manganese present in the soil bears no relation to that of the iron. In the soil on which our wheat samples were grown, the metallic iron found by a mass analysis of the soil was a trifle over 30 times as great as the total amount of manganese. The analytical results given subsequently show that this is not the ratio in which the two elements are present in the kernels and not even in the green plant or in the ripe straw. It does not seem probable that the manganese has been absorbed simply because it existed in the soil associated with iron, if this indeed be the case in any strict sense, for the association might be with calcium as well as with iron.

The method used in determining manganese in grain was to take 10 gm. of ground, air-dried wheat, dissolve it in concentrated nitric acid, and evaporate the solution to a thick, gummy, brown mass. This was then heated over a free flame till all volatile matter was expelled. The dish was then placed in a muffle and most of the carbon burned off. After removal and cooling, a few (4 or 5) cubic centimeters of concentrated sulphuric acid were added. The sides of the dish were washed down with a little water and the solution evaporated at last on a sand bath till vapors of sulphuric acid escaped freely. After cooling, this was taken up with water, boiled, and filtered into a 200 c. c. flask. The residue on the filter was burned, taken up with a little sulphuric acid as before, and the solution filtered and added to the first filtrate. The combined filtrates should be about 150 c. c. in volume and contain about 5 per cent of sulphuric acid. A little silver sulphate (from 25 to 30 mgm.) was next added and then 4 or 5 gm. of ammonic persulphate. The solution was placed on a boiling water bath and allowed to stand as long as the color deepened. It was then cooled, made up to volume, and compared with the standard, which had been prepared in the same way. All reagents should be tested by making a blank.

Manganese in the straw was determined in the same way, except that the silica was removed by evaporating in a platinum dish with the addition of hydrofluoric acid.

In Tables I and II are given the variety, the fertilizer applied, and the percentage of iron and manganese found in wheat from Colorado and

Idaho. Table III gives the percentage of manganese only in wheat from different regions, while Table IV gives the percentage of manganese found in various other grains.

TABLE I.—*Iron and manganese in Colorado wheat*

| Variety. | Fertilizer per acre or other treatment. | Iron. | Manganese. |
|---|---|---|---|
| | | *Per cent.* | *Per cent.* |
| Defiance | 80 pounds of nitrogen | 0.005 | 0.005 |
| Do | 40 pounds of phosphorus | .005 | .004 |
| Do | 150 pounds of potassium | .003 | .004 |
| Do | None | .003 | .004 |
| Red Fife | 80 pounds of nitrogen | .004 | .004 |
| Do | 40 pounds of phosphorus | .004 | .004 |
| Do | 150 pounds of potassium | .004 | .005 |
| Do | None | .005 | .005 |
| Kubanka | 80 pounds of nitrogen | .004 | .005 |
| Do | 40 pounds of phosphorus | .003 | .004 |
| Do | 150 pounds of potassium | .003 | .005 |
| Do | None | .004 | .005 |
| Defiance | Fallowed 1 year | .006 | .005 |
| Marquis | do | .005 | .005 |
| Red Fife | do | .005 | .007 |
| Kubanka [a] | | .003 | .003 |
| Kubanka [b] | | .004 | .004 |

[a] Yellow berry; soft. [b] Flinty; hard.

TABLE II.—*Iron and manganese in Idaho wheat* [a]

| Variety. | Fertilizer per acre. | Water per acre. | Iron. | Manganese. |
|---|---|---|---|---|
| | | *Feet.* | *Per cent.* | *Per cent.* |
| Marquis | None | 1 | 0.006 | 0.006 |
| Do | do | 2 | .005 | .006 |
| Do | do | 3 | .007 | .005 |
| Do | 16 loads of manure | 1 | .006 | .006 |
| Do | do | 2 | .006 | .005 |
| Do | do | 3 | .006 | .005 |

[a] I am indebted to Mr. Don. H. Bark, of Boise, for these samples.

TABLE III.—*Manganese in wheat from different localities* [a]

| Variety. | Locality. | Per cent. | Variety. | Locality. | Per cent. |
|---|---|---|---|---|---|
| Poole | Missouri | 0.007 | Huron | Province of Quebec, Canada. | 0.006 |
| Do | Ohio | .006 | | | |
| Jones's Longberry. | Pennsylvania | .006 | Kubanka | Petrograd, Russia. | .024 |
| Iowa Red | Kansas | .005 | | | |
| Mealy | New York | .008 | Bore | Svalof, Sweden | .004 |
| Red Fife | Province of Manitoba, Canada. | .006 | Wilhelmina | Holland | .004 |

[a] I am under obligation to the respective officers of the various experiment stations for the samples of American and Canadian wheats and to the Bureau of Plant Industry, United States Department of Agriculture, for the samples of foreign wheats.

TABLE IV.—*Manganese in other grains*

| Variety. | Locality. | Per cent. |
|---|---|---|
| Emmer (*Triticum dicoccum*) | Fort Collins, Colo. | 0. 004 |
| Rye (*Secale cereale*) | do. | . 004 |
| Barley, bald (*Hordeum* sp.) | do. | . 002 |
| Oats (*Avena sativa*) | do. | . 005 |

Several samples of corn (*Zea mays*) were tested, a large white variety (Meerschaum) from Missouri, a yellow variety, irrigated, from Grand Junction, Colo., a yellow variety, not irrigated, from Akron, Colo., and a white variety, irrigated, from Fort Collins, Colo. These samples contained so minute a trace of manganese that it could be detected only with great difficulty when 10 gm. of the grain were used for the test.

In addition to the determinations of manganese given in the preceding tables, I have found it uniformly present in the ash of Colorado wheats and also in wheats from California, Nevada, Washington, Montana, South Dakota, Minnesota, Kentucky, and Tennessee. It can, I believe, be accepted as being universally present in the wheat kernel and likewise in the wheat plant, but it is not as abundant in the dried plant as in the kernels. The ratio of the iron to manganese is higher in the plant. The risk of obtaining iron from dust, etc., in the case of the plant is, it is true, greater than in the case of the kernel, but I think that we are fairly safe in assuming that the iron found in our samples belongs to the plant constituents and is not derived from extraneous sources (Table V).

TABLE V.—*Iron and manganese in dried wheat plants*

| Variety. | Date. | Fertilizer per acre. | Iron. | Manganese. |
|---|---|---|---|---|
| | | | *Per cent.* | *Per cent.* |
| Defiance | July 28, 1913 | 120 pounds of nitrogen | ..... | 0. 004 |
| Do. | do. | 60 pounds of phosphorus | 0. 010 | . 003 |
| Do. | do. | 200 pounds of potassium | . 010 | . 003 |
| Red Fife | do. | 60 pounds of phosphorus | . 010 | . 004 |
| Do. | do. | 200 pounds of potassium | . 015 | . 004 |
| Kubanka | Aug. 6, 1914 | 60 pounds of phosphorus | . 008 | . 002 |
| Do. | do. | 200 pounds of potassium | . 013 | . 002 |

Of the preceding samples only the last two were ripe; the others were cut from 8 to 12 days before being ripe enough to harvest.

The iron present in the straws is from two and one-half to six times as great in amount as the manganese, while in the kernels the manganese is approximately equal to the iron and at the same time is higher, as a rule, than in the straw.

The iron was determined gravimetrically in every case and the manganese colorimetrically. The variation in the iron found is great if calculated on the minimum amount found; still the difference between the

minimum and maximum, in spite of the difficulties of the analysis, is only 0.004 per cent, calculated on the air-dried wheat. The quantity of manganese found shows about the same maximum variation, but the determinations are mostly quite uniform without regard to the State or country in which the wheat was grown.

The samples given represent great differences in cultural conditions of both climate and soil, and yet the manganese is always present and in approximately the same quantities; in fact, a greater regularity is found in this respect than for iron in the determinations made. Iron is accepted as an essential constituent of the plant, while the manganese is held to be a nonessential one by most writers.

Bertrand (1), however, has shown that manganous oxid is essential to the action of laccase; and further, that this enzym is universally present in plants and fulfills a definite function in their metabolism, from which he concludes that manganese is an essential mineral constituent of most, if not of all, plants.

The reaction shown when a fresh surface of a potato is treated with a tincture of guaiacum is attributed to the oxidizing action of laccase. If the statements of Bertrand be correct the potato should contain manganese. For this reason I determined the manganese in a potato, using a single tuber, and found the amount of manganese in this potato, which had been dried at 100° C. for 24 hours, to be 0.0003 per cent, corresponding to from 0.00005 to 0.00006 per cent of the fresh tuber. This quantity seems very small, but even much smaller quantities of manganese in nutritive solutions produce decided effects upon vegetation. Brenchley (2, p. 579), in discussing her experiments to determine the effects of manganese upon the growth of barley, says:

> At this date [11 weeks from the beginning of the experiment] it was evident that manganese was deposited in the leaves even at so low a concentration as 1:1,000,000 M. S. and in some cases traces could even be observed in 1:10,000,000 M. S.

The percentages given in my determinations are for elemental manganese; Brenchley used manganous sulphate with five molecules of water. She points out that the effects of manganese may be modified by the relative supply of nutrients.

## SUMMARY

(1) Manganese seems to be present in wheat wherever grown, irrespective of the conditions of soil and climate.

(2) Manganese is present in the wheat kernel in about the same proportion as iron, though iron greatly predominates in soils.

(3) Fertilizers applied to the soil did not affect the amount of manganese stored in the kernels.

(4) Variation in the quantity of water applied, from 1 to 3 feet, did not affect the amount of manganese in the grain.

(5) I do not wish to draw conclusions from my facts relative to the essential character of manganese as a mineral constituent of plants, though these facts seem to support this view for wheat, and possibly for emmer, rye, oats, etc. It seems improbable that a nonessential constituent would occur in all samples and in essentially the same quantity under such a variety of conditions.

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